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ABSTRACT

This document comprises three progress reports for a 5-year environmental aging study aimed at establishing the lifetimes of magnetic tapes and the poly(ethylene terephthalate) (PET) base of photographic and electronic film under archival storage conditions. The first annual report (1982) introduces the rationale for the project, provides background information on PET and a review of selected aging studies involving PET, and describes the scope of the current project. The second annual report (1983) provides the results with PET in the first year as well as descriptions of the second year experiments and their subsequent findings. The progress report (1984) summarizes the two annual reports, discusses their findings, proposes further research, and states conclusions for PET films. Each section of the document contains its own set of references, as well as data tables and graphs which support the study's findings. (JB)

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Prediction of the Long Term Stability of Polyester-Based Recording Media

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Washington, DC 20234

First Annual Report

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PREDICTION OF THE LONG TERM STABILITY OF POLYESTER-BASED RECORDING MEDIA

by

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ABSTRACT

The stability of poly(ethyleneterephthalate) is being studied in order to predict its long term behavior as the base of the film and tape used to record archival information. This report contains results of the first year's work. Film base, with and without photographic and other coatings, was aged at several temperatures and humidities. Mechanical and calorimetric properties and molecular weights were measured at intervals. Degradation was relatively rapid at temperatures of 115, 100, and 85 °C at 100% relative humidity. The scission rate at 85 °C was about 10^{-6} mol scission/g-day and the activation energy was 113 kJ/mol. Rates decreased strongly with relative humidity, becoming negligible in dry air and nitrogen. At 55 °C and 100% relative humidity degradation was not significant in 163 days. Samples were seriously embrittled by the introduction of about one scission per molecule--about 10^{-4} mol scission/g. In its present state, gel permeation chromatography probably is not precise enough to be a good degradation monitor, since one would like to know when degradation had exceeded a fraction of the damaging level. Differential scanning calorimetry showed little change in melting behavior of samples aged at 55 and 85 °C. Glassy samples crystallized during aging at 85 °C but not at 55 °C.

Magnetic tapes based on poly(ethylene terephthalate) usually have a polyester polyurethane binder that holds the magnetic particles. The binder is thought to be more sensitive to hydrolysis than the tape base. Results obtained with a thermoplastic polyester polyurethane imply that there may be an equilibrium extent of degradation for any storage condition. At 20 °C and 50% relative humidity, about 70 x 10^{-5} mol scissions/g might occur. The corresponding molecular weight is only 1400 and it is expected that binder of this molecular weight would be too soft.

It is anticipated that the study will go on for four more years. Agings at 35 °C at several humidities are going on and samples will be examined at intervals. Attempts will be made to develop more sensitive methods to detect degradation.

Key Words: degradation; film base; hydrolysis; photographic film; polyester; poly(ethylene terephthalate); recording media; stability

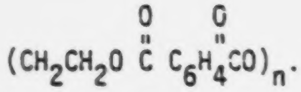
1.0 Introduction

Many of the cultural, historic, and commercial records are now kept in forms other than that of the traditional paper books or documents. Tapes for audio, video, or digitally encoded information as well as microfilm are increasingly popular storage media because of their higher storage density and their compatibility with automated data access and retrieval systems. Newer electrographic imaging systems combine the advantages of microfilm with the ability to update pages, thereby totally eliminating the need for paper records even for active files.

Poly(ethylene terephthalate) (PET) is the supporting base in much of the photographic film and most of the magnetic tape that is used to record archival information. The lifetime of PET is unknown under conditions of archival storage. Similarly, polyester polyurethane binder, used to hold magnetic particles on magnetic tapes, has an unknown lifetime.

Over twenty years ago, similar considerations prompted the Library of Congress, with support from the Rockefeller Foundation, to sponsor a study of the archival qualities of phonograph discs and the types of magnetic tapes available at that time. The report of that study, "Preservation and Storage of Sound Recordings" by A. G. Pickett and M. M. Lemcoe, contains a discussion of the probable modes of deterioration of those recording media and recommendations for storage conditions that still seem reasonable today. The present study was begun in 1981 under the sponsorship of the National Archives. It begins a five-year program aimed at producing measurement methods and data for predicting the lifetimes of polyester-based materials under archival storage conditions. It is hoped that the results will be general enough to be applicable to the products which will be available during the next ten to twenty years and is therefore not merely an assessment of the stability of specific current products. This report describes the results of the first year of the study.

2.0 Background

2.1 PET. This polymer has the chemical structure,  $(CH_2CH_2O\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}O)_n$. Industrial production has been described recently [1]. Currently the polymer is made from dimethyl terephthalate by catalyzed ester exchange with ethylene glycol. Two exchange steps are involved. In the first, bis (hydroxyethyl) terephathalate is formed at about 150-200 °C and methanol is distilled off. Reaction catalysts are acetates of cobalt, magnesium or zinc. PET is formed in the second step by heating the first product to 280 °C with antimony trioxide. Ethylene glycol is formed, which is removed under vacuum, thereby favoring polymer formation. At 280 °C, residual catalyst from the first step would convert some ethylene glycol to bis-(hydroxyethyl) ether. This could enter the polymer through ester exchange and affect its properties. To prevent this, phosphoric acid or triphenyl phosphate is added along with the antimony trioxide. These complex the acetate catalysts and render them innocuous.

Recently high purity terephthalic acid has become available in large quantities and may become the starting material of choice. In this process bis-(hydroxyethyl) terephthalate would be made directly from terephthalic acid and ethylene glycol, using titanium alkoxides or dialkyl tin oxides or carboxylates. With these present, conversion of bis (hydroxyethyl) terephthalate to PET does not require antimony trioxide, although some may be used.

Storage qualities of the finished product may be affected by the process used. Specifically, since catalysts must act on forward and reverse reactions, residual esterification catalyst will promote hydrolysis. If the catalyst is destroyed by side reactions (hydrolysis, for example) the residual activity may not be great. In a study of the hydrolysis of poly(butylene adipate) glycol we found that it hydrolyzed with a smaller rate constant if it had been prepared without catalyst.

A side reaction that occurs during polymerization of PET may also be important to its subsequent storage qualities. This is the self disproportionation of the polymer chain to form vinyl (-- $CH = CH_2$) and acid ($HO \overset{O}{\overset{\|}{C}} C_6H_4 CO$--) end groups. Hydrolysis of esters is known to be acid catalyzed so manufacturers strive to keep the acid content low. Acid concentrations of 15-50 μ eq/g are typical of commercial polymers [2].

The number (M_n) and weight (M_w) average molecular weights of commercial PET are about 20,000 and 45,000 g/mol respectively. About 1.3-1.8 wt. %

of cyclic compounds-dimers, trimer, tetramer, and pentamer, are present. The most abundant is a cyclic trimer [2,3]. Conceivably, these compounds may migrate out of the polymer in prolonged or high temperature agings, affecting physical properties and the measured M_n.

PET is weak, brittle, and opaque unless subjected to a complex thermomechanical treatment [2] to be described. Polymer is heated above the melting temperature, T_m (about 250 °C), extruded, and quenched. Then it is heated to about 135 °C (the glass temperature, T_g, is about 70 °C) and stretched biaxially. Subsequently the polymer is heated to about 150 °C, under restraint, and some crystallization occurs. It is then cooled and may be "tensilized" by stretching it unidirectionally. The result is a clear film with a tensile strength as high as 200 MPa (30,000 psi) and an elongation at break of about 150%. Although the film is quite clear, the amount of crystallinity is appreciable--from 30 to 50% is estimated by calorimetry.

Glassy PET, prepared by simply melting and quenching the polymer, is clear but is weaker and less deformable than fully treated film. Therefore, the tremendous improvement in mechanical properties brought about by the thermomechanical treatment is due to residual orientation and stress in the film. The presence of residual stress is shown by the two fold shrinkage in length and width that occurs if a film is heated quickly to 285 °C.

Temperatures in previous aging studies of PET have generally been above T_g in order to keep aging times from becoming unreasonably long. Archival storage temperatures are normally of the order of 20 °C or below [4].

Thus a rather rather long extrapolation below T_g is required when applying previous data to the temperature region of interest. There is no convincing evidence that such extrapolation is valid. Indeed, one anticipates some discontinuity at T_g because of changes in mobility. Thus, above T_g one would expect that a scission in an amorphous portion of a polymer chain would be followed by rapid relaxation of any strained configurations that portion had. Considerably below T_g one would expect the broken chain would maintain its strained configuration. Presumably there should be differences in physical characteristics that reflect such contrasting behavior that would not be taken into account by simple extrapolation through T_g.

There have been several aging studies involving PET. We will not attempt to review all but will describe the most important ones. The reaction of primary interest is ester hydrolysis, which breaks the polymer chain generating acid and alcohol groups, i.e. $H_2O + -CO_2- \rightarrow -CO_2H + HO-$.

One of the most thorough of the previous studies is that by McMahon et al. [5]. The hydrolysis of PET was studied at temperatures between 130 and 50 °C at relative humidities, RH, of 0, 20, 50, 75, 95, and 100%. Samples consisted of 0.5 and 10.0 mil-thick film, the former more oriented than the latter, and 1100 denier yarn. The maximum time was 300 days. The amount of chain scission, calculated as the fraction of ester groups hydrolyzed, was deduced from intrinsic viscosities. Measurements were also made of tensile strength, elongation and density. Infra-red spectra were studied.

Plots of the amount of chain scission versus time showed upward curvature. However, this became appreciable only after samples had become brittle so rate constants for chain scission were taken as the initial slopes. For the 0.5 mil sheet these were approximately proportional to RH at constant temperature and had an activation energy of about 110 k J/mole, independent of RH. Rate constants for the 10- mil sheet increased more rapidly than relative humidity but were 1/4 to 1/2 those of the 0.5 mil sheet. The activation energy was about 120 kJ/mol. It was assumed that diffusion limited the degradation rate of the 10 mil sheet. The yarn, which had threads thinner than 0.5 mil, was considerably more stable than either sheet. Possibly orientation and/or crystallinity contributed to these rate differences.

The 0.5-mil and 10-mil films were judged to have failed when 0.7 and 0.5% of the ester groups had been hydrolyzed, respectively, which amounts to about one ester group broken per molecule. Extrapolation by the Arrhenius equation gave lifetimes of about 500 and 800 years, respectively, for these films at 25 °C, 50% RH.

The lowest temperature at which work was reported is 60 °C. In 300 days at 100% relative humidity the intrinsic viscosity had decreased from 0.53 to 0.45 dL/g. The decrease was approximately uniform with time. The value of T_g in such a long experiment may be less than 70 °C, so it is uncertain if this degradation is below T_g.

Arguments were given [5] to the effect that degradation due to thermal or oxidative scission is about three orders of magnitude less than hydrolytic scission at 100% RH. The data for films at 90 °C in dry air initially showed a small decrease in intrinsic viscosity followed by an increase to about the initial value.

During degradation of the films there were increases in density, attributed to increases in crystallinity, and also increases in absorbance at 3425 cm^{-1}, attributed to incorporation of -OH groups in the polymer.

A more recent paper described hydrolysis at 100 °C, 100% RH [6]. Carboxylic acid contents were measured at various times for samples having different initial acid contents. These data show clearly that degradation is autocatalytic, the rate increasing proportionally to initial acid content and exponentially with time. Since acid contents of the samples studied by McMahon et al. [5] were not given, it is possible that some of the differences between samples were due to differing initial acid contents.

The above studies did not involve film bearing photographic emulsions, which might affect the degradation. Adelstein and McCrea [7,8] have aged photographic film and also uncoated film base.

Samples were sheets of base, 4 mil thick in the case of PET and also sheets of exposed and developed photographic film, on the same thickness of base. Most of these were preconditioned at 21 °C, 50% RH and then sealed in 2.5 cm diameter glass tubes, about 100 sheets of one kind to each tube. The volume of the tube was made small to minimize evaporation of moisture from the samples. The samples were then placed in ovens at temperatures between 71 and 125 °C for various times. Properties measured included intrinsic viscosity, tensile strength and elongation, emulsion melting and image loss, and brittleness on rapidly bending the film. The last two are qualitative tests.

The results for the first three properties were assumed to obey first order kinetics and rate constants were calculated as the fraction of each property lost per unit time. These rate constants were not used directly in extrapolation but instead were used to calculate times to 20% viscosity loss, 10% loss in tensile strength, and 10% loss in elongation at break. Times to emulsion melting and image loss and onset of brittleness were also judged. These times were extrapolated by the Arrhenius equation to 21 °C. The extrapolated times range from 1000 to 2000 years. Relative humidities at each temperature are unknown and must be different, so the reliability of the extrapolation appears questionable.

Longer experiments were done in which samples were aged at 25 °C - 60% RH, 38 °C -78% RH, and 50 °C - 20% RH for times up to 24 years. After 24 years at 25 °C, 60% RH decreases in intrinsic viscosity and elongation were 3% and 22% respectively; tensile strength appeared to increase slightly, about 5%. The extrapolation described above predicts that in 24 years losses of these three properties will be 0.1, 0.2, and 0.4% respectively at 25 °C. Thus the extrapolation described above predicts rather different changes in properties than were observed.

PET base with a photographic emulsion layer degraded about three times faster than the uncoated support. This was attributed to production of ammonia from the gelatin. Ammonia is known to attack PET quite severely [2]. However, to us it seems that the effect might also be due to humidity differences, since gelatin which sorbs water strongly at 21 °C, might desorb it at oven temperatures. Relative humidities would be greater in these tubes. At high temperature the film with the cellulose triacetate base appears somewhat more stable than the film with the PET base. Below 100 °C this situation is reversed.

2.2 Magnetic Tape. Most magnetic tapes consist of a thin (0.25-1.50 mil) PET substrate with a front coating containing a magnetic material, commonly $\gamma\ Fe_2O_3$ or CrO_2. The magnetic material is embedded in a polymeric binder. Common binders are based on polyester polyurethanes. Sometimes there is a carbon coating on the back, which is also embedded in a polymeric binder. The carbon coating dissipates electrostatic charge.

The polyester polyurethane binders used on tapes are highly cross-linked materials with complex structures. They can be expected to have 5 - 10 times as many ester groups as urethane groups. Aliphatic esters are used; these are more susceptable to hydrolytic degradation than the PET substrate. Thus the degradation of interest in magnetic tapes is primarily that of the binder. On degradation this softens; adjacent layers of tape may stick together or the binder may stick to the recording heads. Ultimately the tape becomes unreadable.

The hydrolytic degradation of soluble aliphatic polyester polyurethanes is quite well understood [9,10]. The reaction proceeds by the equation:

$$H_2O + -CO_2- \xrightarrow{k} -CO_2H(A) + HO- \qquad (1)$$

Here an ester link, $-CO_2-$, reacts with water, breaking the polymer chain and giving an alcohol and a carboxylic acid (A), which catalyzes the reaction. Typically there are about 10^{-2} mol ester groups for one gram of polymer. If 5 - 10% of these are hydrolyzed the polyurethane molecular weight becomes about 1000 - 2000 g/mol. This is far too low to have the mechanical properties of a polymer. Thus severe property degradation can occur without much change in the ester concentration. For any sample, the water content is determined by the relative humidity and the temperature and is not much affected by the extent of degradation. Consequently, ester and water concentrations can be included in the rate constant, k. Scissions in mol/g are equal to the change in the reciprocal of the number average molecular weight, $\Delta(M_n^{-1})$. This equals the change in acid content. Since the reaction is acid catalyzed the applicable differential equations are:

$$\frac{d[A]}{dt} = \frac{d\,\Delta(M_n^{-1})}{dt} = k[A] \qquad (2)$$

where t is time and k is the fractional rate of increase in acid concentration. After integration:

$$[A] = [A_o]e^{kt} \qquad (3)$$

$$\Delta(M_n^{-1}) = [A_o]\,(e^{kt}-1) \qquad (4)$$

where $[A_o]$ is the initial acid content, about 10^{-5}eq/g.

For polyester polyurethanes based on polycaprolactones and polybutylene adipates, k was approximately proportional to relative humidity and, at 100% RH, increased with temperature with an activation energy of about 75 kJ/mol [10].

Carbodiimides are sometimes used as hydrolysis stabilizers in polyester polyurethanes because they react with acid, reducing reaction 1 to negligible proportions. However, there is a slow uncatalyzed hydrolysis, ordinarily negligible, which continually generates acid [11]. This reacts with carbodiimide, eventually consuming it. Subsequently, reaction 1 again becomes significant and destroys the polymer.

Esterification, the reverse of hydrolysis, may be significant at low relative humidities. If k^1 is the rate constant for the reverse of reaction (1) then the rate of ester formation will be $k^1\,[A]^2[HO-]$. The acid concentration is squared because acid was a catalyst for the forward reaction and so must be one for the back reaction. If hydrolysis has occurred to a moderate extent, [A] and the [HO-] will be about equal, since $[A_0]$ is small and acid and alcohol form at equal rates. Thus a sample undergoing degradation at low RH ought to reach an equilibrium described by the equations:

$$k[A] = k\,^1[A]^3 \text{ or } k = k\,^1[A]^2 \quad (5)$$

At 35°C, 100% RH, unstabilized, soluble polyester polyurethanes lasted about 400 - 500 days before becoming very weak. Highly cross-linked materials would be expected to last longer because more scissions would be required to reduce the molecular weight to a critical value. Such samples have been examined. Cross-linked reticulated foams, taken from airplane fuel tanks, have been studied by preaging them until soluble and then aging them for additional periods to measure the rate of increase in acid content [12]. The rate data were extrapolated backward in time to get the acid contents before aging. These correlated well with mechanical properties and the times (5 - 8 years) the materials had been in service. The actual rate constants were about equal to those of soluble polyurethanes.

Two studies have been concerned with the hydrolytic stability of magnetic tape binder. E. F. Cuddihy measured the weight of acetone-soluble components and evaluated the adhesion between binders and PET [13]. Agings were done in air and in nitrogen at relative humidities of 0, 11, 30, and 100% at temperatures of 36, 48, 61, and 75 °C. Samples that had been hermetically sealed at relative humidities of 30, 60, and

100% at each temperature were also aged. The weight of the acetone soluble materials decreased at 0 and 11% RH and in all the hermetically sealed samples, indicating that crosslinking occurred. The other samples showed increases in sol fraction. These increases were attributed to scissions caused by hydrolysis. The crosslinking was attributed to the reverse process, esterification.

The adhesive strength between binder and PET was estimated by rubbing the tape with a swab that had been soaked in tetrahydrofuran and measuring the time required to dislodge the binder layer. Values were 14±2 seconds for unaged tape. They ranged down to as little as one second for a sample aged 14 weeks at 75 °C, 100% RH and up to 30 seconds for samples aged 14 weeks in dry air or nitrogen at 75 °C. Thus the results parallel the sol fraction observations.

The crosslinking effect found for hermetically sealed samples is puzzling since the samples were supposedly equilibrated at humidities high enough to cause degradation. Thus, unless the binder initially had considerable acid and alcohol, one would expect that the sol fraction would increase and the humidity decrease until hydrolysis and esterification went on at equal rates. Relative humidity was measured in several experiments and found to increase. As noted above, sol fractions decreased. Possibly the iron oxide particles contain some $Fe(OH)_3$, which reacted with carboxylic acid to give water and an iron carboxylate.

Cuddihy concluded that at a relative humidity of 24% at 21 °C the binder should be stable, neither crosslinking nor degrading.

The second study of tape stability was undertaken for the U.S. Air Force [14]. The effect of humid aging was only part of the study; much of the effort went into mechanical characteristics of tape winding and their effect on long term tape readability.

To study the effect of humidity, reading error rates were measured before and after aging tapes at: 55 °C, 100% RH; 20 °C, 50% RH; and 20 °C in a hemetically sealed container (conditions at closure were not stated). Tapes were examined at three month intervals for 12 - 15 months. Low density and high density multitrack systems were used. At 20 °C it was concluded that the error rate increased somewhat but remained small, about one error in 10^6 to 10^7 bits. However there were some unreadable blocks and tracks, usually on the outer part of the reel or on the outer edge of the tape, that were eliminated from consideration. At 55 °C there was severe binder degradation, to the point where binder flaked off the tape if it was stretched. Reading difficulties started after six months of aging and became worse. However, with the multitrack system, information could be recovered after 15 months aging at 55 °C, 100% RH by combining results from several tracks.

The authors of the report were aware of the Cuddihy work and attempted to use it to calculate a relative humidity-temperature line along which there would be no hydrolysis. However, they set up the equilibrium as $k = k^1[A]$, which appears contrary to the law of mass action. Consequently, their recommended storage conditions, 18 °C at 40% RH, are suspect in our estimation. Our own experience with a variety of polyester polyurethane elastomers suggests that considerable degradation would occur under such conditions, but we have no experience yet with tape binder.

3.0 Present Approach

3.1 PET. Samples of several materials are being aged at 25, 50, and 100% relative humidity at 35, 55, and 85 °C. In addition to two exposed and developed photographic films, there are samples of two electrographic systems, some uncoated PET film base, and NBS 1470, a PET film having known permeation characteristics. Samples for each condition are in one large test tube closed with a rubber stopper. The samples are suspended on a frame above the LiCl humidifying solution. In addition, samples of the leader are being aged in sealed tubes under dry air, dry nitrogen, and nitrogen at 100% RH. The coating has been removed from some of the commercial samples in order to get results with and without coatings. At 35°C some samples contain test patterns in order to see effects on the gelatin layer.

Samples are removed at intervals, tested for brittleness by creasing, and their molecular weights are determined by gel permeation chromatography. Tensile strengths, TS, and elongation, E, are measured in many cases. A differential scanning calorimeter (DSC) is used to observe glass and melting behavior and measure ΔH_f, the heat of fusion. A potentiometric titrator has been received and acid contents will be determined. Some infrared measurements were made and more are planned.

Two sets of smaller scale experiments are being run. These involve glassy samples and samples preaged at 85 °C, 100% RH. These are being aged only at 100% RH, the last set only at 55 °C and 35 °C.

Properties of unaged samples are in Table I. The first three materials (all photographic products) and coated electrographic film D have similar properties. Other materials have somewhat lower values of M_n and TS and higher values of ΔH_f. Values between 113 and 144 J/g have been estimated [15] for 100% crystalline PET, so our samples appear to be 30-50% crystalline by calorimetry.

Uncoated electrographic film C has particulary high values of ΔH_f and E and a low value of TS. It "necks" in the tensile tester suggesting that it was not prestretched as much as the other materials.

The lower molecular weights of the glassy polymer indicate that it degraded during preparation. When heated in the calorimeter it exhibits a strong glass transition, then crystallizes, and finally melts. This behavior is shown later. Pieces of the glassy polymer were small and contained bubbles. Consequently, their tensile properties were not measured.

3.2 Tapes. To date we have not aged magnetic tapes but have been studying equilibrium characteristics of esterfication at different humidities and temperatures. Materials studied include a polyester polyurethane elastomer and several polyester diols used to make polyester polyurethanes.

4.0 Results

4.1 PET

4.1.1 Mechanical Properties. Table II lists the number of days of aging after which samples cracked when creased, a qualitative test designated "Finger Brittleness." These times depend on humidity and temperature. No failures have yet been observed in samples aged at 85 °C, 25% RH or at 55 °C. At 85 °C, 100% RH, approximately 100 days cause failure of all samples. Electrographic film C was embrittled more rapidly than the others.

Figures 1 and 2 show elongation at break as a function of aging time at 85 °C. The figures show effects of surrounding gas, relative humidity, and removal of any coating. The lines indicate the general trends of the data. At 100% RH almost all elongation is lost between 80 and 100 days, whether in air or in nitrogen, whether coated or not. Specimens of uncoated and coated electrographic film C, aged at 100% RH, were not run in the tensile tester. The former was too brittle to handle after 61 days, at which time only a small piece of the latter was taken. After 81 days the latter was too brittle to handle. At 50, 25, and 0% RH all samples show progressively less loss of elongation.

Figures 3 and 4 show tensile strength as a function of aging time at 85 °C. Decreases on aging are not nearly as severe as found for elongation. The influence of humidity and the lack of any consistent difference associated with the presence of a coating are qualitatively as found with elongation.

4.1.2 Chain Scissions in PET. Molecular weights were measured by use of gel permeation chromatography using four microstyragel columns having pore sizes 10^1, 10^2, 10^2, and 10^4 nm. The solvent was hexafluoroisopropanol containing 0.01 M sodium trifluoroacetate. This salt tends to prevent adsorption of polymer on the packing. Calibration was performed by using published chromatograms and intrinsic viscosities of PET in hexafluorisopropanol [16] to calculate the Mark Houwink equation between intrinsic viscosity and molecular weight at the chromatogram peak. This relationship was assumed valid for our polymers. Then we determined the intrinsic viscosities and chromatographed several of our degraded and undergraded samples. Use of the Mark Houwink equation gave molecular weight at the peak as a function of retention volume on our column set.

This calibration technique is being used on a tentative basis. Efforts were also made to develop a calibration with a better theoretical basis. Narrow fractions of polymethyl-methacrylate were purchased and a universal calibration was developed (polystyrene is insoluble in hexafluroisopropanol and so could not be used). When applied to PET this calibration gave values between 3000 and 200 for undegraded and degraded samples and thus was seriously in error. The reason for the failure is unknown. Also, in our preliminary work we found that metastable solutions of PET could be formed by dissolving it first in hexafluoroisopropanol and then diluting 30 fold with chloroform. These solutions were stable for

7-10 days and so could be chromatographed. The mixed solvent, being effectively chloroform, dissolved polystyrene fractions, which were chromatographed and the results made the basis of a universal calibration. When applied to PET the result was as above, unbelievably low molecular weights.

Several chromatograms of degraded and undegraded PET in hexafluoroisopropanol are in Figure 5. The secondary maximum at about 37 cm^3 was found with all materials. The progressive shift of the peak maxima to higher retention volumes as aging time increases means that the molecular weight decreases on aging. Aging at 100 °C and 115 °C for short times caused severe degradation. There are small peaks at higher retention volumes than shown here, 40 - 60 cm^3. These are observed if polymer-free solvent is injected and so are ignored.

The molecular weights are calculated from the chromatograms by assuming that the height above the baseline is proportional to the concentration of polymer, whose molecular weight is determined from the retention volume at which that height occurs. Therefore, the weight fraction of polymer in a certain molecular weight range is proportional to that fraction of the total area under the chromatogram between certain retention volumes. A digital computer is used to make the necessary summations and calculate M_w and M_n.

One characteristic of the results is that M_n is quite sensitive to location of the baseline. This is shown in Fig. 6, which gives M_w and M_n for two baseline locations. The location of the baseline is really somewhat subjective, particularly in the low molecular weight region because of the solvent impurities and because there is probably some adsorption of the polymer on the column packing. The larger standard deviation found for M_n than M_w in table I for film base reflects this situation.

In calculating scissions, M_n is the quantity of interest because M_n^{-1} represents mol polymer per gram. Therefore $\Delta(M_n^{-1})$ is the increase in mol polymer per gram. This is equal to the mol of scissions per gram, since each scission adds one to the number of polymer molecules. Probably $\Delta(M_n^{-1})$ is uncertain by about 2×10^{-5} mol scission per gram.

Figures 7 and 8 are plots of $\Delta(M_n^{-1})$ versus time at 85 °C. At 100% RH a linear extrapolation of $\Delta(M_n^{-1})$ at longer times to zero time falls below the origin, suggesting that the scission rates increase with time; the line is drawn so as to emphasize this trend. The scatter is great and it is thought there are no significant differences in scission rates between samples. This is true even of coated and uncoated electrographic films C despite their early mechanical failures, compared with those of the other samples. At 100 days there is about 6×10^{-5} mol scission/g, indicating that values of M_n have been reduced from about 17000 to 8000. Thus, there has been about one scission per original molecule at failure, in agreement with the work of McMahon et al. [5]. Degradation is much less at 50, 25, and 0% RH.

Figure 9 shows scissions formed in the glassy polymer at 100% RH at 85 °C and also at 55 °C. At 85 °C the scission rate is about four times as large as with the other samples. At 55 °C the number of scissions is negligible.

Table III shows results from a variety of samples aged at 55 °C, 100% RH for 163 days. No property decreases very much and some increase slightly. Consequently, we have as yet no evidence of degradation at 55 °C.

Single aging experiments were done in sealed tubes at higher temperatures than 85 °C. At 115 °C there were 26×10^{-5} mol scissions/g in 13 days and at 100 °C there were 22×10^{-5} mol scissions/g in 39 days. At 85 °C at 100% RH there were 11 x 10^{-5} mol scission/g in 123 days. Overall rates are plotted in Fig. 10. The activation energy is about 113 k J/mol or 27 kcal/mol in reasonable agreement with 29 kcal/mol found by McMahon et al. [5]. Their rates at 85 °C, 100% RH are about 2 x 10^{-6} and 10^{-6} mol scissions/g, day for 0.5 mil and 10 mil film, respectively. Our value for the same conditions is 0.9 x 10^{-6} mol scissions/g, day.

4.1.3 Calorimetry with PET. Some scans between 45 and 180 °C from the differential scanning calorimeter are in fig. 11. For each curve the starting ordinate value is arbitrary and the slope is made approximately zero. The curves for the unaged commercial samples show deflections at about 75 °C that are indicative of glass temperatures, although they are very weak. That for unaged film base is typical of most of our materials. The deflection for the uncoated electrographic film C is the largest for any of the commercial samples. Aged samples do not show a normal T_g but their curves appear to have weak melting peaks about 30-45 degrees above the aging temperature. Interpretation will not be attempted now because the effects of time, humidity, and extent of degradation are unknown.

Curves for the same polymer and also for some aged NBS 1470 between 180 and 280 °C are in Fig .12; the ordinate sensitivity is one tenth that in Fig. 11. Curves 1 and 2 cover the range found for unaged polymers except for the glassy one. The temperatures at the peak maxima, T max, and the heats of fusion are listed in Table IV. Long heating does not affect these quantities much at 55 °C and 85 °C. The changes with samples aged at 100 °C and 115 °C probably are significant.

Fig. 13 and 14 show calorimeter scans for the glassy material. The ordinate scales are both made the same as in Fig. 12 in order to keep the crystallization peaks on scale. The transition at T_g for unaged glassy material is much stronger than for the other unaged materials. Aging at

85 °C permits crystallization, which greatly reduces the size of the glass transition and eliminates crystallization during the scan. Aging at 55 °C did not cause crystallization but it did shift the glass transition temperature. It is encouraging that crystallization did not occur since this process might destroy the orientation of commercial films.

4.2 Polyester Polyurethanes. Cuddihy's work suggests that hydrolysis of polyester polyurethane tape binder may be equilibrium limited at low relative humidity [13]. Binder insolubility and the presence of iron oxide prevent reliable kinetic analysis so we made a preliminary study of equilibrium using soluble polyester polyurethane and polyester diols. In this study hydrolysis was followed by measuring the acid content as a function of time.

A thermoplastic polycaprolactone polyurethane elastomer with an initial acid content of 10^{-5} eq/g was aged at 85 °C, 100% RH until the acid content was 25.5×10^{-5} eq/g. Portions of this material were then re-aged at 85 °C at relative humidites of 27, 12, and 0%. The variation in acid content during the re-aging experiments is shown in Fig. 15. At 27 and 12% RH the equilibrium acid contents are 60 and 35×10^{-5} eq/g, respectively. Samples were also aged at 8% RH at 55 °C and at 11% RH at 35 °C. Equilibrium acid contents were 33 and 28×10^{-5} eq/g respectively. Thus equilibrium acid contents change little with temperature at the same relative humidity.

Polyester diols were also equilibrated at 85 °C and nominal relative humidities of 95, 50, and 25%. At 85 °C these materials are liquids with viscosities of about 30 Pa.s (300 cp). [A] in eq/g of poly(butylene adipate) and poly(caprolactone) diols at equilibrium were 3.9×10^{-3} and 3.2×10^{-3} at 95% RH, 1.4×10^{-3} and 1.2×10^{-3} at 50 % RH, and 0.6×10^{-3} [poly(butyleneadipate)] at 25% RH. The equilibration is now being studied at 55 °C and it appears that the equilibria [A] are not much different from those at 85 °C at the same relative humidity.

Rate constants for the hydrolysis are known from previous work [10]. Therefore, rate constants for the back reaction can be calculated, by equation 5 for the polyurethane and by its modification for the polyester diols. Modification is required because the polyester diols initially contain about 10^{-3} eq/g of -OH groups; consequently [A] and [-OH] are not equal. Secondly, at high relative humidity the ester concentration is changed by hydrolysis. The equation is:

$$\frac{k[E]}{[E_0]} = k^1[A]([-OH_0] + [A]) \qquad (6)$$

Here $[E_0]$ and $[-OH_0]$ are initial concentrations of ester and -OH groups and E is the equilibrium concentration of ester. At equilibrium, $[A] >> [A_0]$, so that the [-OH] is nearly equal to $([-OH_0] + [A])$. $[E_0]$ and $[-OH_0]$ are known characteristics, being 10^{-2} and 2.1×10^{-3} eq/g, respectively, for poly(butyleneadipate) diol and 8.77×10^{-3} and 10^{-3} eq/g, respectively, for the poly(caprolactone) diol.

At 0% RH there is no hydrolysis so k^1 for the polyurethane was calculated from the kinetic data for this condition in Fig. 15. If third order kinetics are assumed then k^1 is half the slope of $[A]^{-2}$ versus time. The three points fit third order kinetics rather well (Fig. 15, x's and dashed line).

The values of k^1 are listed in Table V. As humidity increases k^1 decreases for all three materials. The polyester diols have smaller k^1 values than the polyester polyurethane.

The k^1 at about 10% RH for the polyurethane were extrapolated to 20 °C by the Arrhenius relation to obtain 1.2×10^3 $g^2/eq^2 \times$ day. The corresponding value of k, obtained by extrapolating data in reference [10], is 1.2×10^{-4} day^{-1}. If these rate constants are substituted in eq. (5) the equilibrium acid content is calculated to be 32×10^{-5} eq/g, about as observed at 85 - 35 °C at this humidity. If one neglects any change in k^1 with relative humidity and takes k as being proportional to relative humidity then the equilibrium acid content will vary as the square root of the relative humidity ratios, giving 50 x 10^{-5} and 70 x 10^{-5} eq/g at 25 and 50% RH at 20 °C. The reticulated foams studied earlier had lost substantially all their tensile strength at acid contents of 22 x 10^{-5} and 36 x 10^{-5} eq/g. About 65% of the strength was retained at 9 x 10^{-5} eq acid/g.

Alternatively, one can neglect equilibrium and use k to calculate the time to reach some limiting acid content from the initial acid content, which is probably about 10^{-5} eq/g. Values of k are 3 x 10^{-4} and 6 x 10^{-4} day^{-1} at 25 and 50% RH at 20 °C. If the limiting acid content is 15 x 10^{-5} eq/g then, by solving eq. (3) for t, one obtains times equal to about 25 and 12 years respectively for the above conditions.

These calculations were all based on data from a thermoplastic polyester polyurethane and it is not known how closely they will apply to tape binders. The ideas should be valid for any aliphatic polyester polyurethane and modifications exist if stabilizers are present [11].

5.0 Discussion

5.1 PET. The degradation observed is consistent with previous work and supports the idea that the most likely cause of degradation under ordinary conditions will be hydrolysis. It is somewhat surprising that serious loss in physical properties occurs with only one scission per molecule. However the molecular weight of the polymer is quite low so one scission per molecule may bring M_n below a critical value. In addition, the highly oriented nature of the material may furnish an explanation. One picture of a strained semicrystalline polymer is that much of the stress is carried by strained amorphous portions of chains that tie crystalline regions together [17]. Another concept is that mechanically strained bonds are sensitive to chemical attack [18]. If one combines these ideas then the attack would tend to be localized at bonds that are critical for mechanical strength.

The results with the glassy material appear somewhat in conflict with these ideas, since nominally unoriented, glassy polymer degraded faster than the oriented PET. However, the DSC results indicate that the sample crystallized during aging. This might have had some effect because the degradation that occurred during heating prior to forming the glass probably introduced acid groups, which would be expected to have a catalytic effect on hydrolysis. Being on chain ends, they would probably be located preferentially in non-crystalline regions.

In the coming year the agings at 55 °C and 35 °C will be continued and others will be started at 70 °C. Acid contents will be measured by use of a potentiometric titrator, which was delivered recently. Some agings will be also be started in the presence of small concentrations of sulfur dioxide and nitrogen oxides. These may be environmentally significant for the degradation since the concentration of acid pollutants is likely to increase as lower grade fuels become more common.

Finding that severe mechanical degradation requires very little chemical degradation has made us rather skeptical of the value of gel chromatography as a method of monitoring samples, unless the precision of the measurements can be improved by a factor of ten or more. Infrared methods will be investigated more thoroughly in an effort to find a sensitive means for detecting degradation. Other methods to be considered are transmission of sound and light [19].

5.2 Magnetic Tape. Two problems involved in studying degradation of tape binder are the presence of crosslinks and iron oxide. The latter may represent 80% of the coating. Methods employed will be like those used to study crosslinked foams--pre-aging to render the binder soluble, additional aging, and then determination of the acid contents. Filtration or centrifugation will be used to remove the iron oxide particles. Infrared spectroscopy will also be used to get evidence for reaction between binder and iron oxide.

Experiments will be carried out at several temperatures and humidities. The hydrolysis of tape binder is expected to be much more rapid than that of PET.

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Table I. Properties of Unaged PET[1]

	$10^{-4}M_w$ g/mol	$10^{-4}M_n$ g/mol	TS, M Pa	E, %	ΔH_f, J/g
Uncoated Film Base	4.90 ±0.11	1.77 ±0.34	204 ±5[2]	144 ±8	47 ±3
Microfilm A	5.04	2.15	200 ±14	126 ±13	48
Microfilm B	4.80	1.69	193 ±11	122 ±11	48
Encapsulating Film	4.16	1.59	177 ±22	80 ±15	56
Uncoated Electrographic Film C	4.20	1.44	116 ±7	185 ±22	59
Coated Electrographic Film C	4.07	1.54	167 ±5	105 ±7	55
Coated Electrographic Film D[3]	4.60	1.68	201 ±10	99 ±16	47
PET Film NBS 1470[4]	4.50	1.45	150 ±11	96 ±29	54
PET, NBS 1470 Glassy Polymer[5]	2.60	0.88	--	--	-32 56

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[1] Samples 0.01 cm (4 mil) thick except as indicated. Uncertainties are standard deviations of three or more measurements.

[2] 1 M PA = 145 psi

[3] 4.8 mil

[4] 1 mil

[5] Made by heating and quenching NBS 1470. About 10 mil thick.

Table II. Days Aging of PET at 85 °C to Induce Finger Brittleness

Material	100% RH	50% RH
Film Base	105	>146
Microfilm A	97	>146
Microfilm B	97	>146
Encapsulating Film	105	>146
Uncoated Electrographic Film C	61	81
Coated Electrographic Film C	81	146
Coated Electrographic Film D	>81	>84
PET Film NBS 1470	90	--

Table III. Percentage Change in Properties of PET Aged at 55 °C, 100% RH, for 163 days

Material	M_w	M_n	TS	E
Film Base	0	10	-8	-8
Microfilm A	-8	-2	-3	+10
Microfilm B	-2	28	6	6
Uncoated Electrographic Film C	-7	15	-9	12
Coated Electrographic Film C	3	20	-9	-2
Encapsulating Film	-1	28	6	6
Arithmetic Mean	-2.5	15	-5.3	9

Table IV. Effect of Aging on T_{Max} and ΔH_f

Material	Aging Conditions			T_{Max}, °C	ΔH_f, J/g
	°C	days	%RH		
Film Base		Unaged		251 ±0[1]	47 ±3[1]
Film Base	55	163	100	252	49
Film Base	85	154	25	252	46
Film Base	85	105	100	253	52
Uncoated Electrographic Film C		Unaged		260	59
Uncoated Electrographic Film C	55	163	100	257	65
Uncoated Electrographic Film C	85	154	25	257	62
NBS 1470		Unaged		255	54
NBS 1470	55	90	100	254	52
NBS 1470	85	39	100	255	48
NBS 1470	85	60	100	253	53
NBS 1470	85	90	100	255	59
NBS 1470	100	39	100	249	64
NBS 1470	115	13	100	243	62

---

[1] Uncertainties are standard deviations of three measurements.

Table V. Rate Constants for Esterfication

Material	Temp./°C	RH/%	$10^{-5}k^1/g^2/eq^2\cdot day$
Poly(caprolactone) polyurethane	85	0	4.1
Poly(caprolactone) polyurethane	85	12	1.9
Poly(caprolactone) polyurethane	85	27	1.4
Poly(caprolactone) polyurethane	55	8	0.17
Poly(caprolactone) polyurethane	35	11	0.06
Poly(caprolactone) diol	85	50	0.47
Poly(caprolactone) diol	85	95	0.13
Poly(butyleneadipate) diol	85	25	0.42
Poly(butyleneadipate) diol	85	50	0.26
Poly(butyleneadipate) diol	85	95	0.07

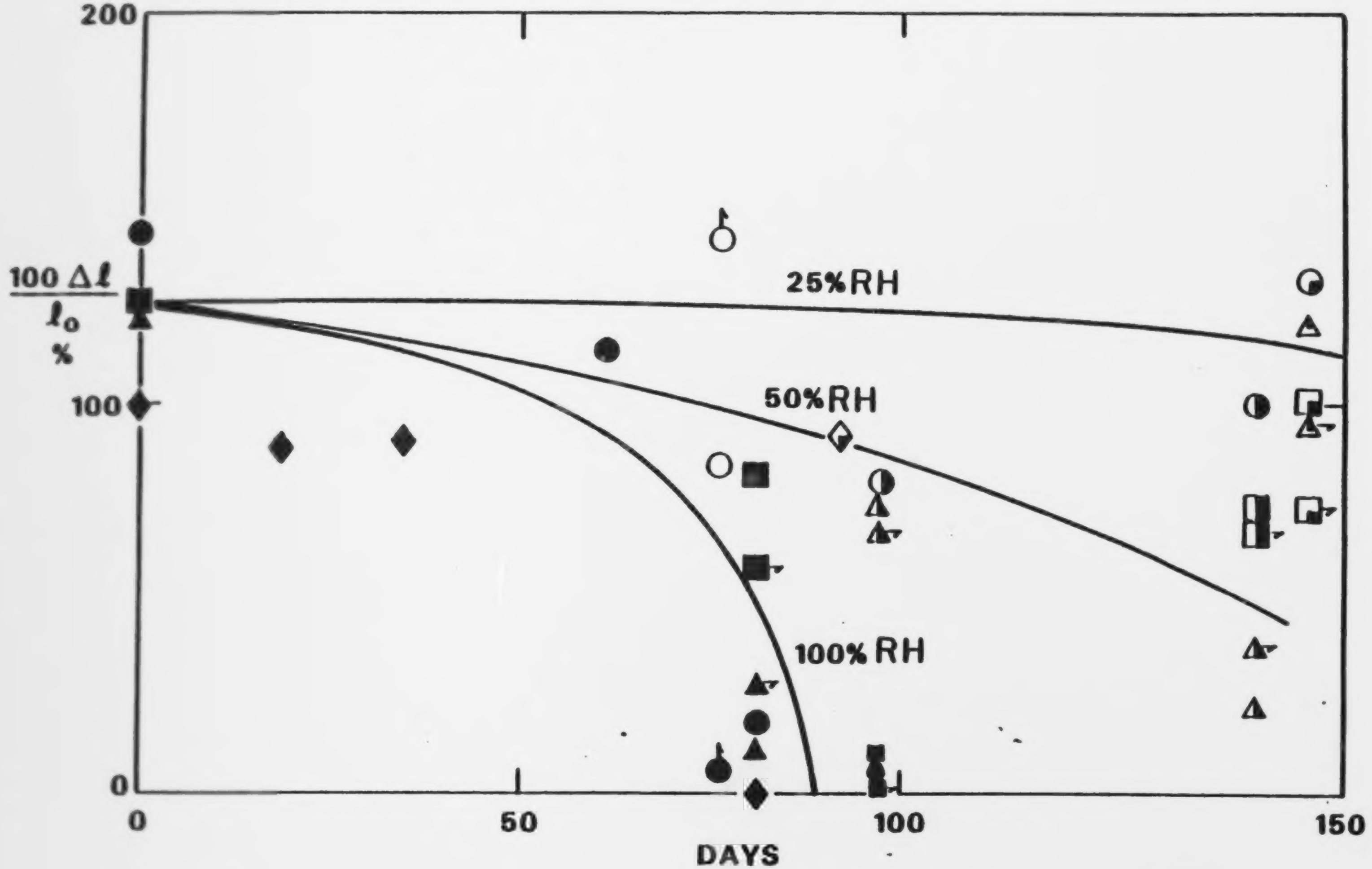


Fig. 1. Elongation at break versus aging time at 85 °C. ○, ◔, ◑, ● film base; ◱, ◧, ■, microfilm A; △, ◭, ▲ microfilm B; ◆, coated electrographic film D. Shadings indicate relative humidity: Unshaded, 0%, quarter shaded, 25%; half shaded 50%; fully shaded, 100%; flags indicate special exposure condition: horizontal, gelatin-layer removed; vertical, under N_2.

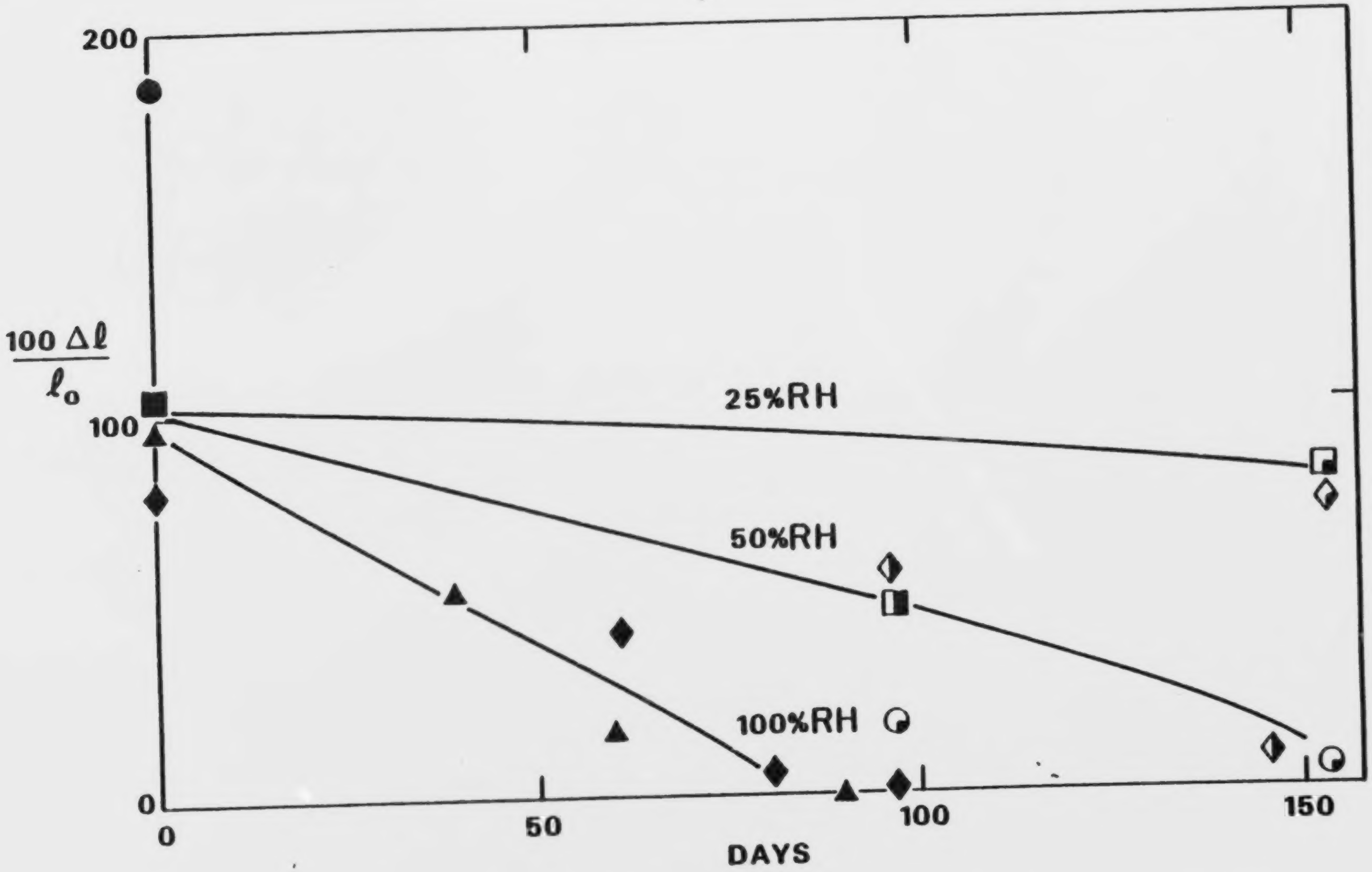


Fig. 2. Elongation at break versus aging time at 85 °C. ◔, ● uncoated electrographic film C; ◲, ◨, ■ coated electrographic film C; ▲, NBS 1470; ◇, ◈, ◆ encapsulating film. Shading code as in Fig. 1.

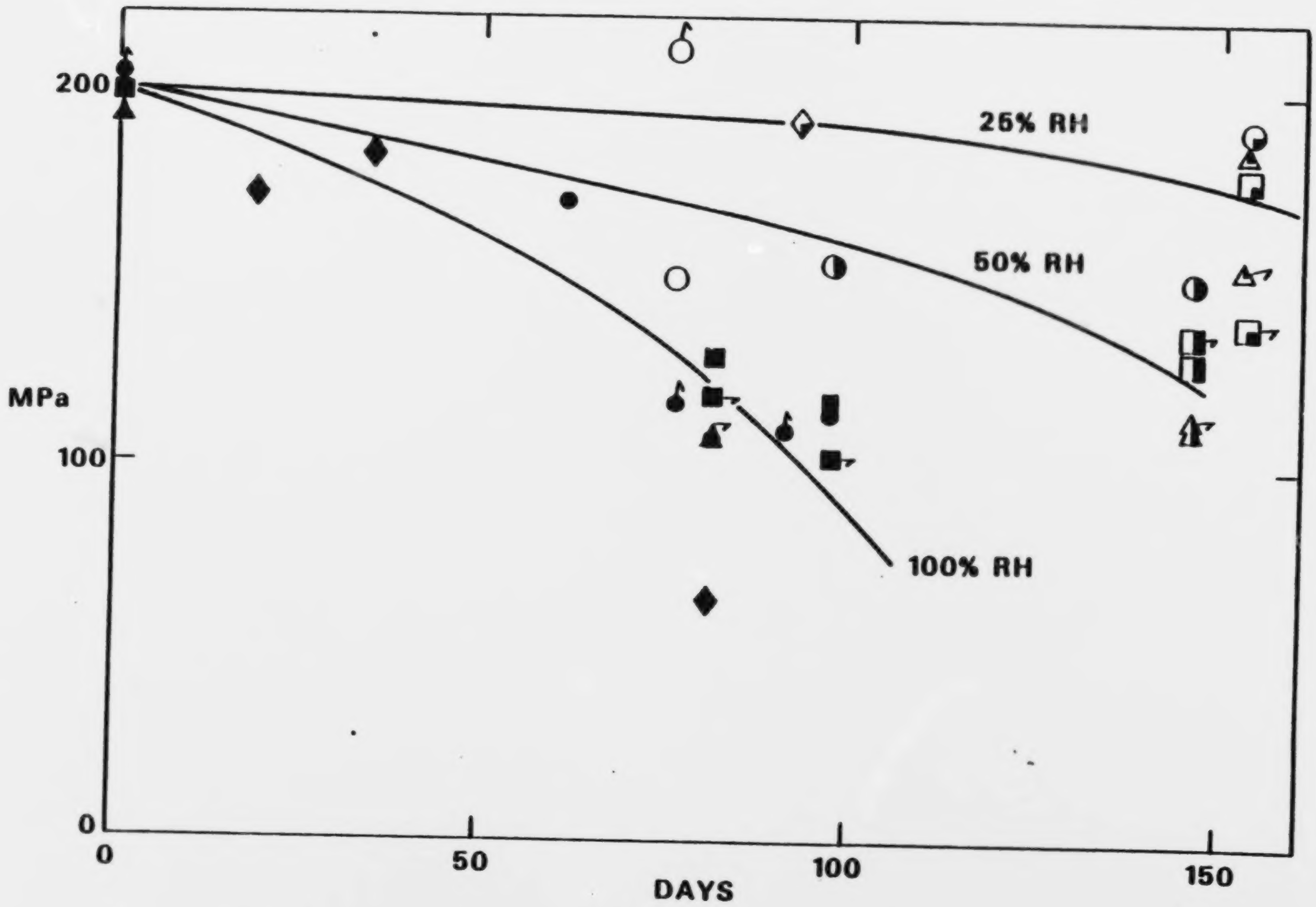


Fig. 3. Tensile strength versus aging time at 85 °C. ○, ◒, ◑, ● film base; ◰, ◧, ■ microfilm A; △, ◭, ▲ microfilm B; ◇, ◈ coated electrographic film D. Shadings and flags as in Figure 1.

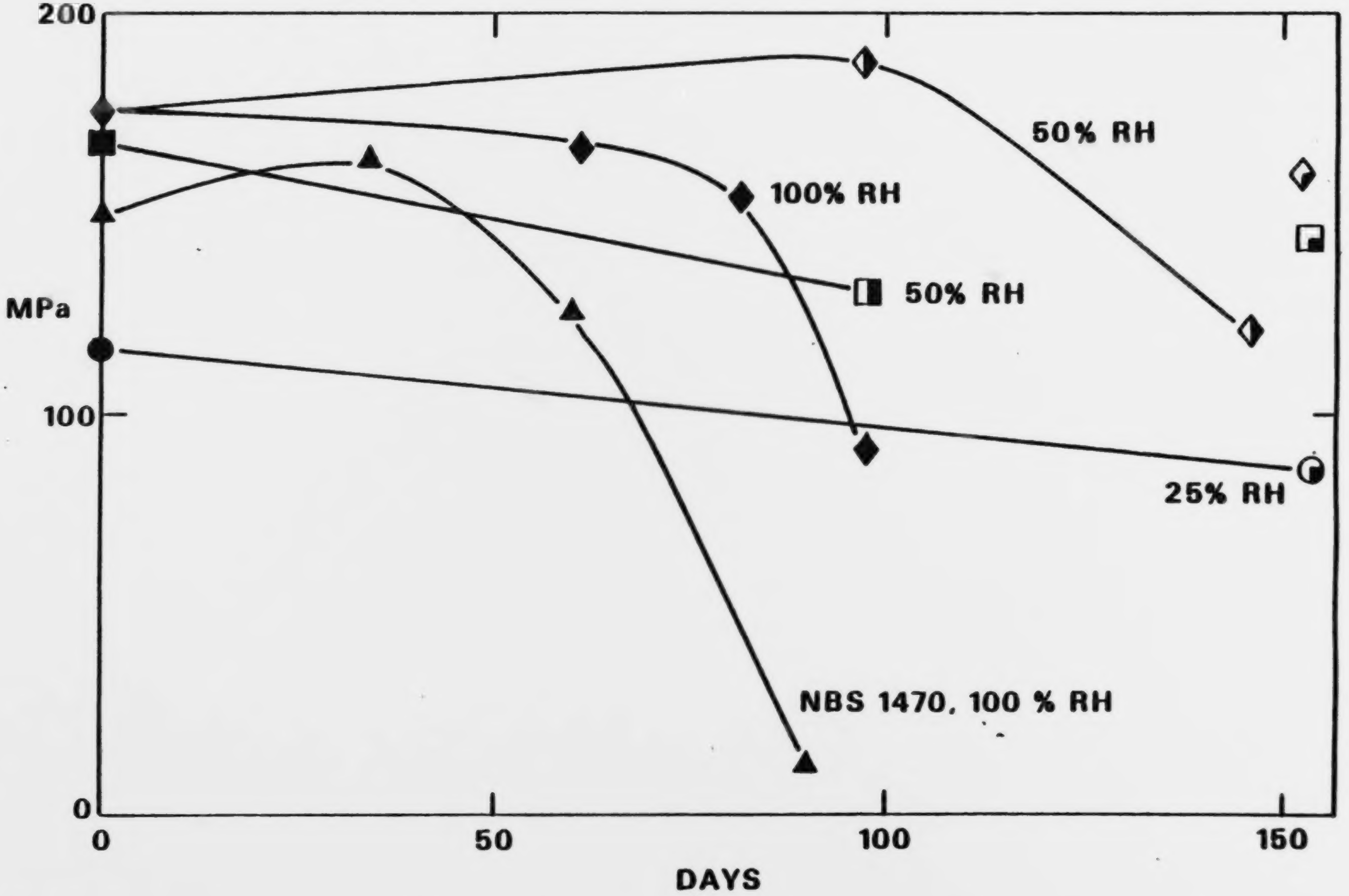
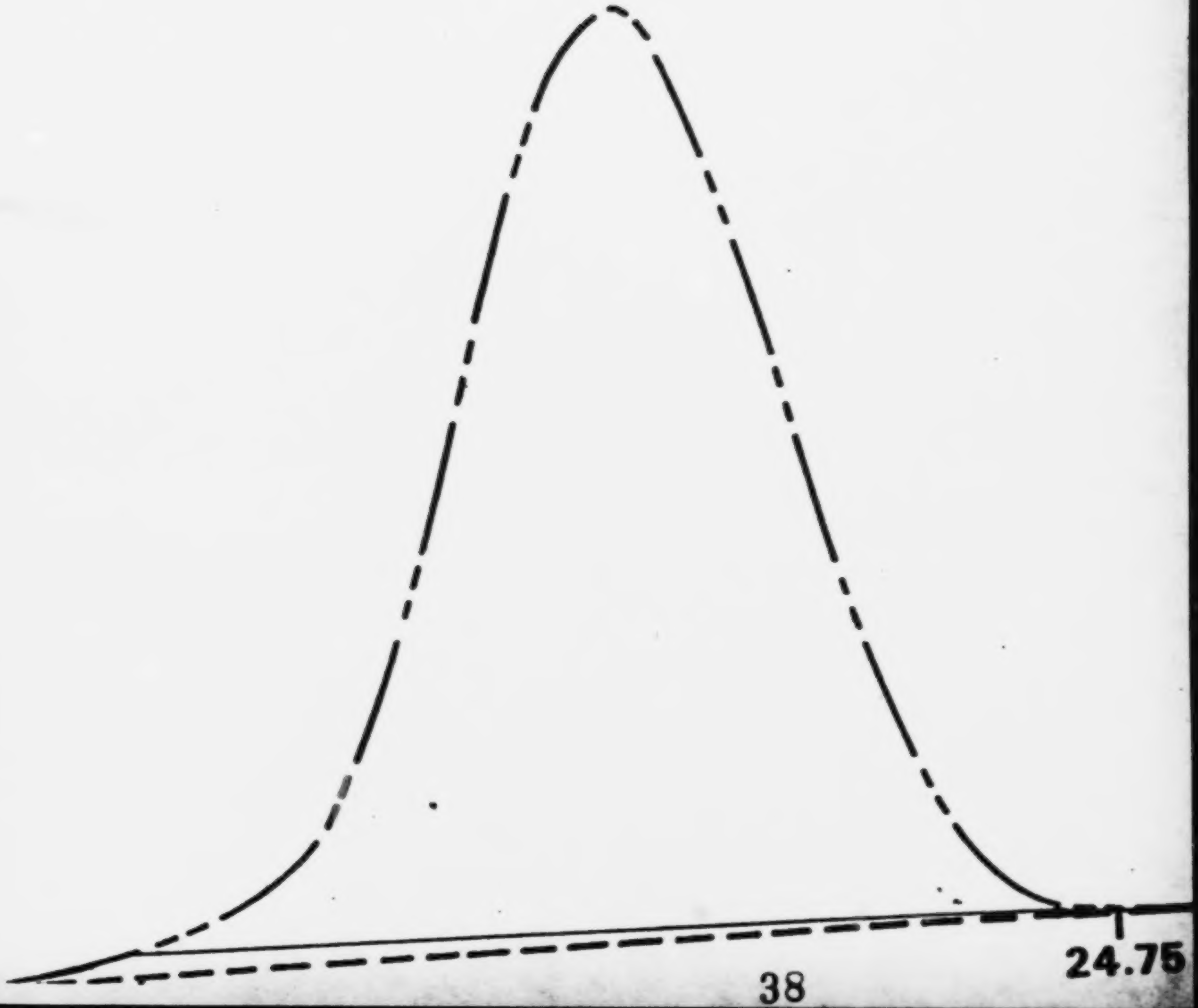


Fig. 4. Tensile strength versus aging time at 85 °C. ◐, ●, uncoated electrographic film C; ◪, ◨, ■ coated electrographic film C; ▲, NBS 1470; ◇, ◈, ◆ encapsulating film. Shading code as in figure 1.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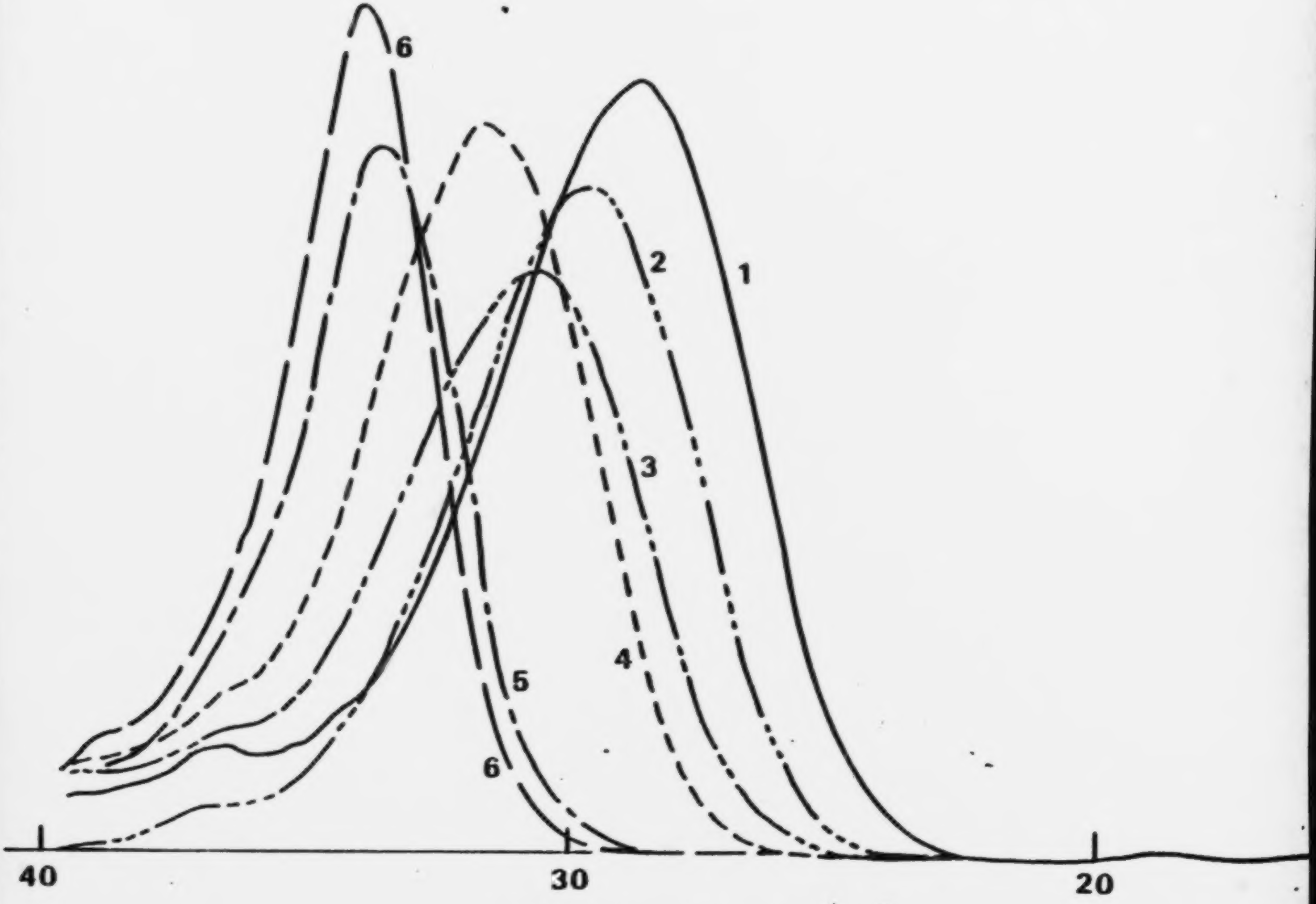

Fig. 5. Gel permeation chromatograms of NBS 1470 unaged and aged at 100% RH. Curve; 1, unaged; 2, 85°, 39 days; 3, 85°, 60 days; 4, 85°, 90 days; 5, 100°, 39 days; 6, 115°, 13 days.

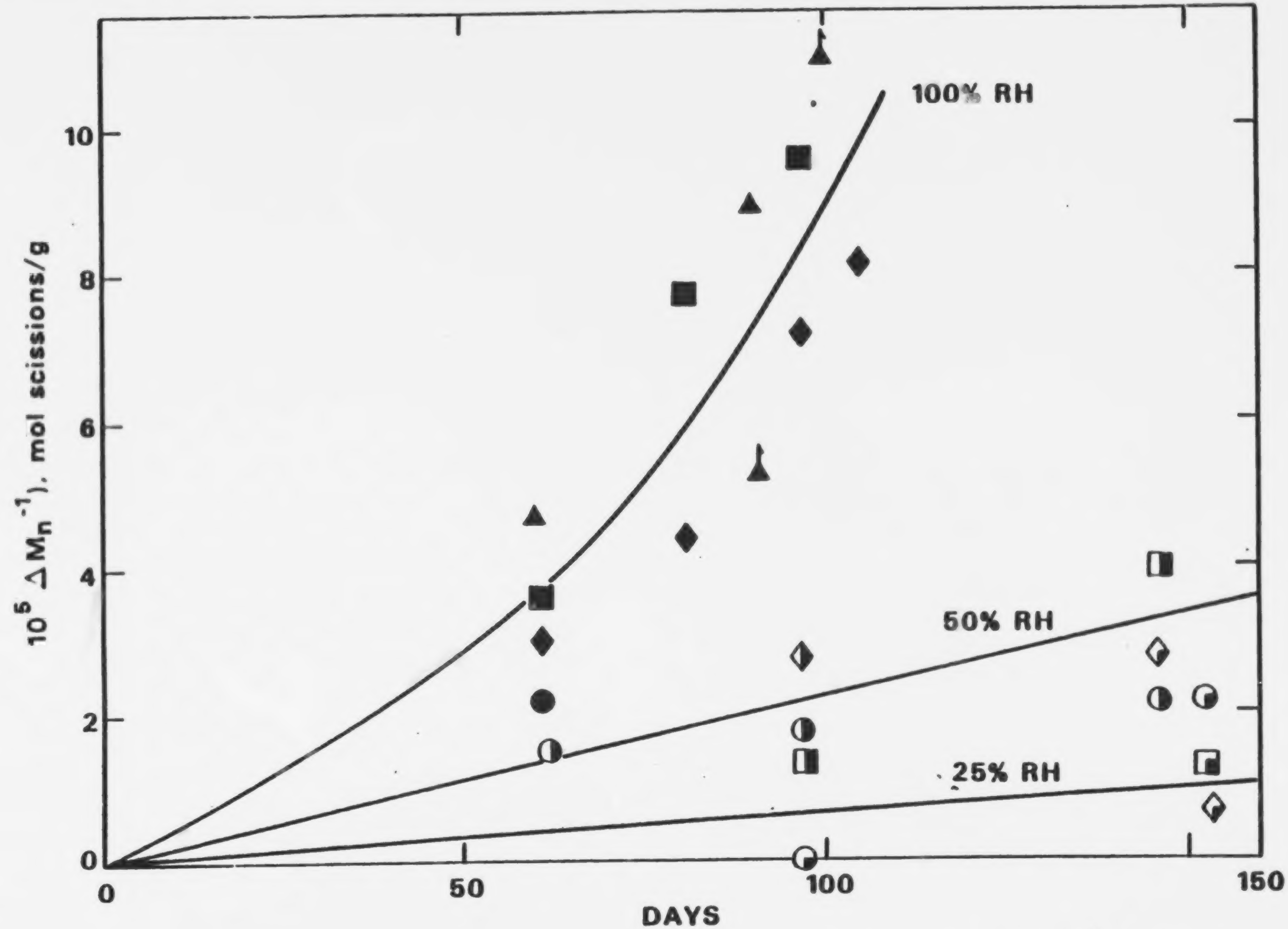

Fig. 8. Chain scissions versus aging time at 85 °C. ○, ◐, ● uncoated electrographic film C; ◻, ◧, ■ coated electrographic film C; ▲ NBS 1470; ◊, ◈, ◆ encapsulating film. Shading and flags as in figure 1.

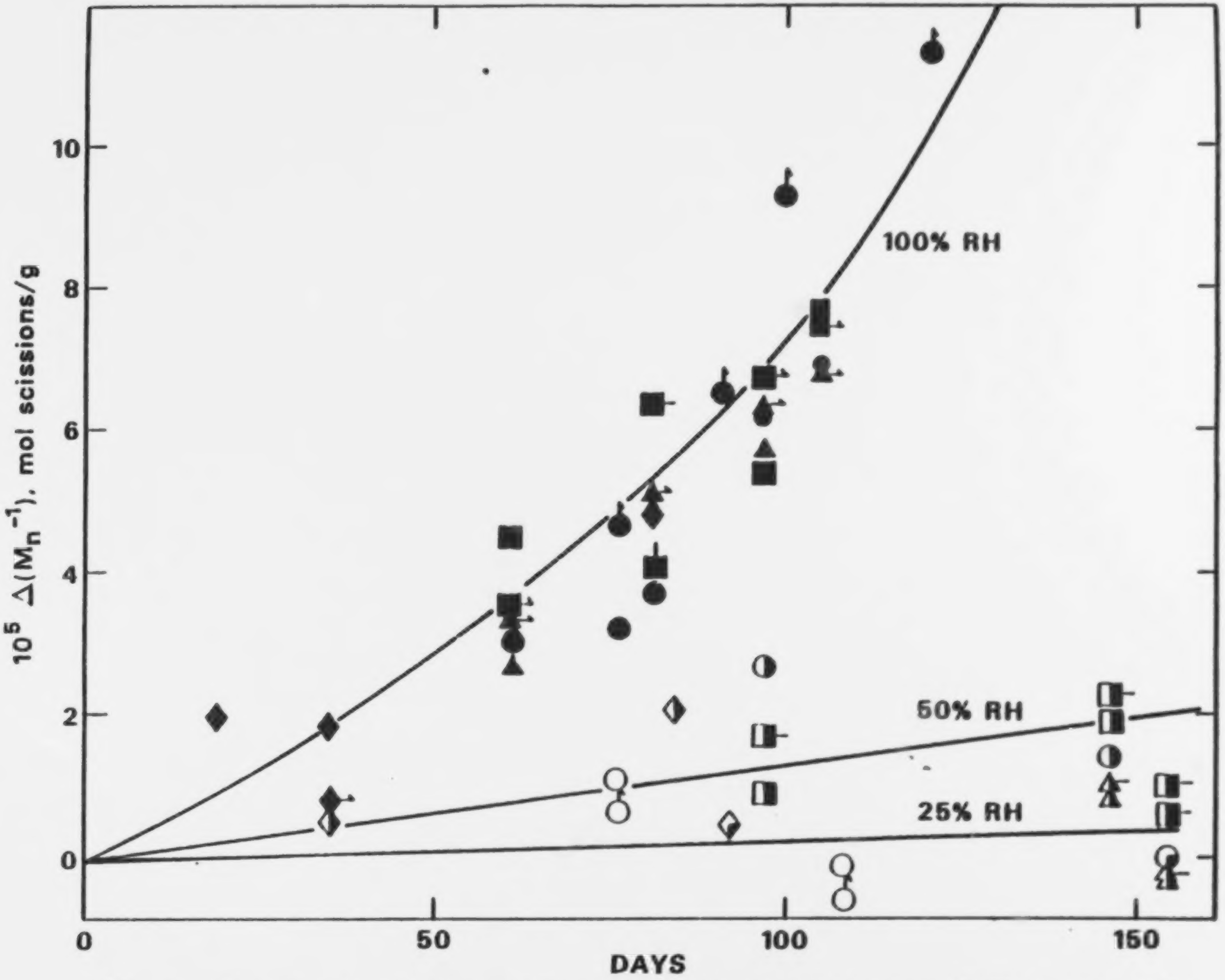

Fig. 7. Chain scissions versus aging time at 85 °C ○, ◐, ◑, ● film base; ◧, ■ microfilm A; △, ▲ microfilm B; ◇, ◈, ◆ coated electrographic film D. Shading and flags as in Figure 1.

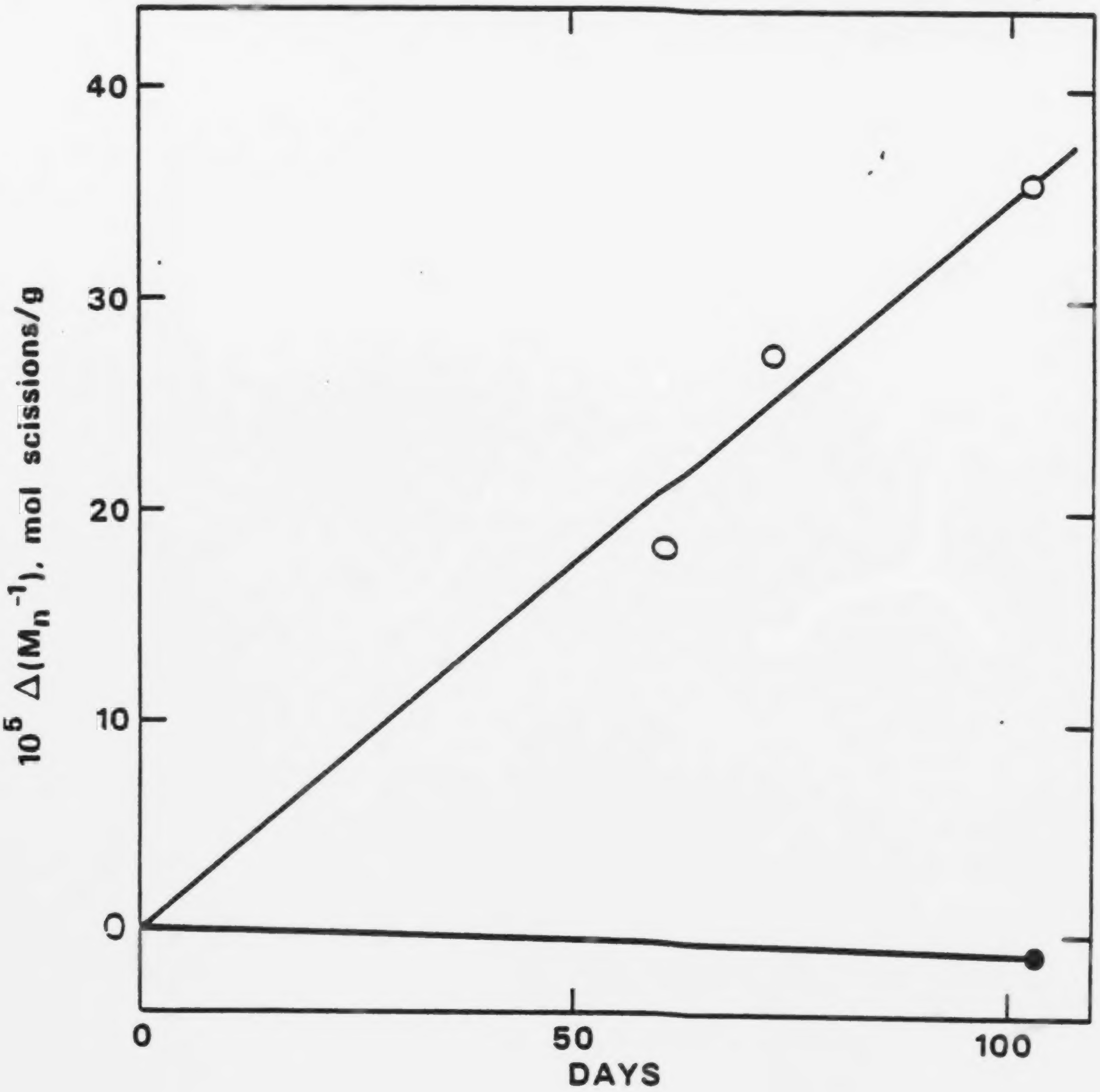

Fig. 9. Chain scissions in glassy PET made from NBS 1470. O, 85 °C, 100% RH; ●, 55 °C, 100% RH.

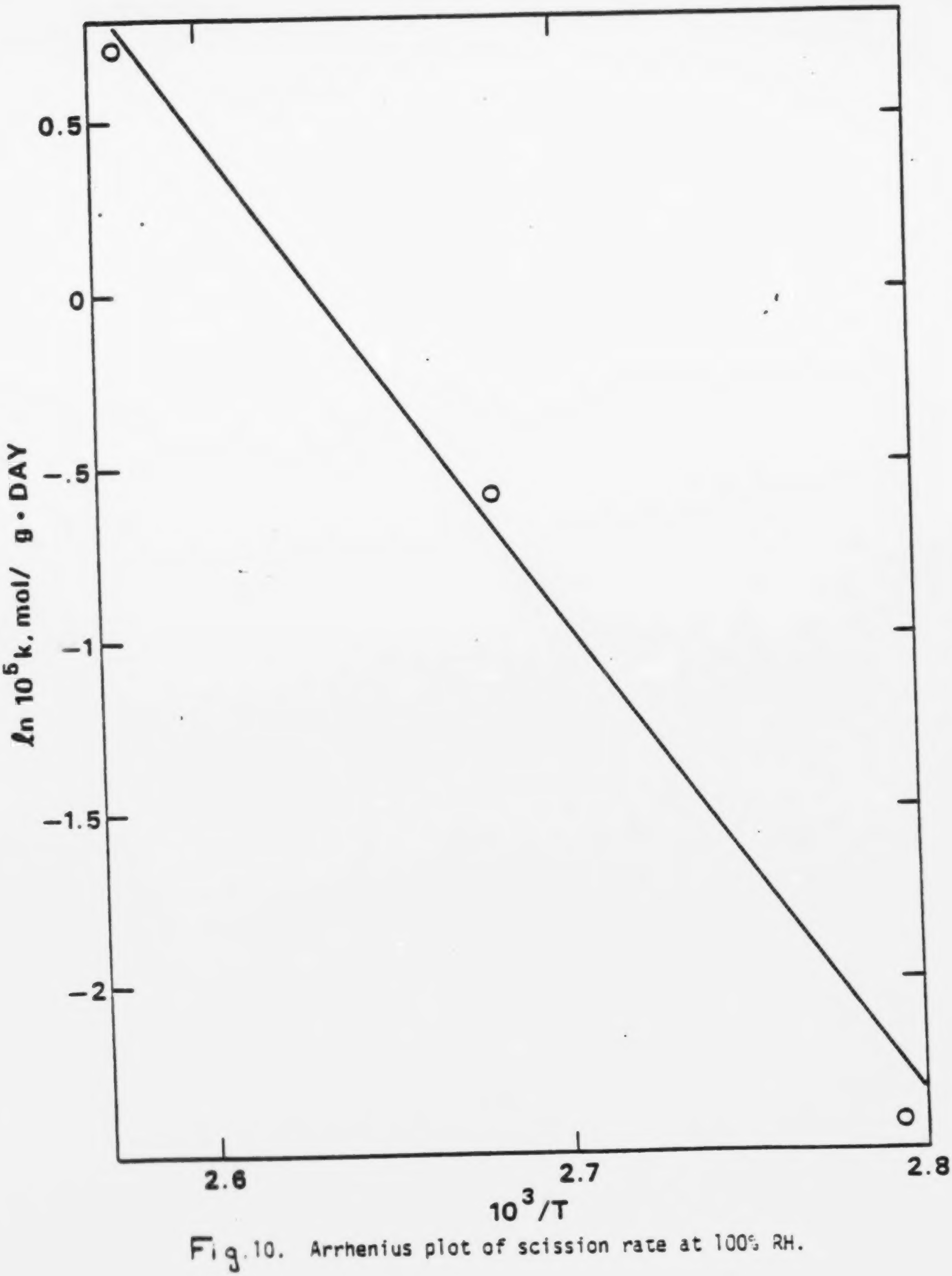

Fig. 10. Arrhenius plot of scission rate at 100% RH.

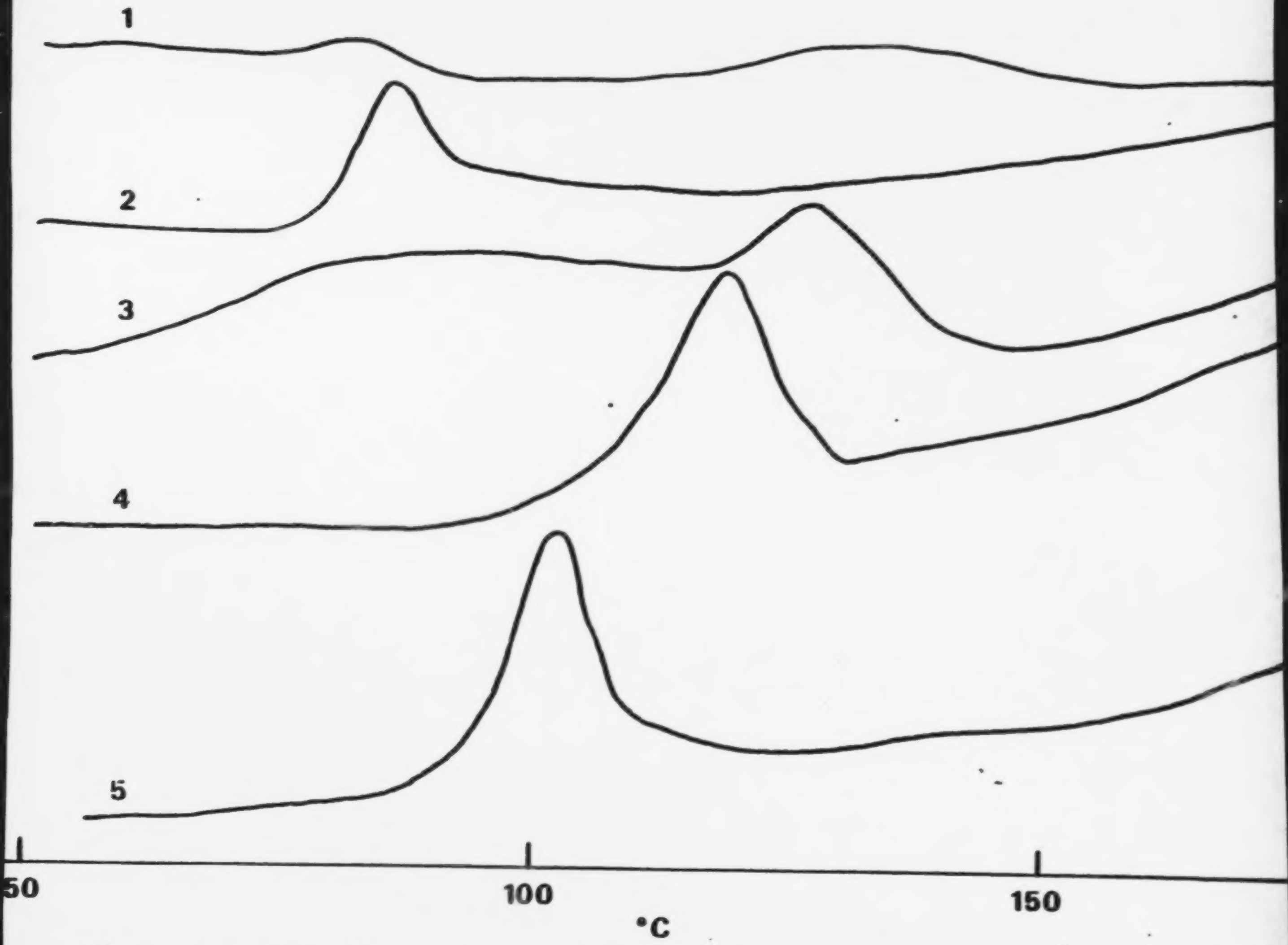

Fig. 11. Differential scanning calorimeter curves. 1, unaged film base; 2, unaged uncoated electrographic film C; 3, film base aged 85 °C, 100% RH, 105 days, 4, film base aged 85 °C, 25% RH, 154 days; 5 , film base aged 55 °C, 100% RH, 163 days.

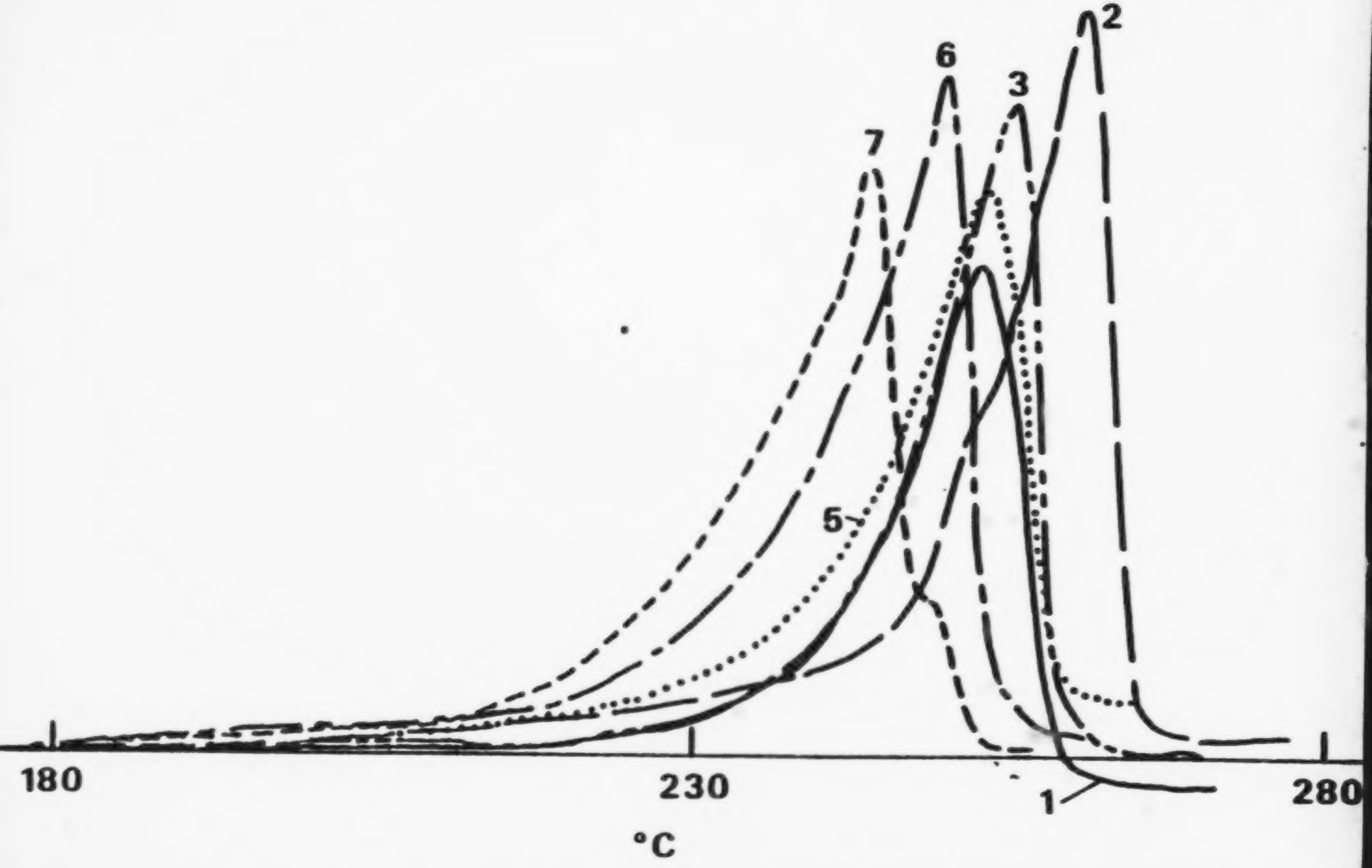

Fig. 12. Differential scanning calorimeter curves. 1), unaged film base; 2, unaged clear electrographic film C; 3, film base aged 85 °C, 100% RH, 105 days; 5, film base aged 55 °C, 100% RH, 163 days; 6, NBS 1470 film, aged 100 °C, 100% RH, 39 days; 7, NBS 1470 film, aged 115 °C, 100% RH, 13 days.

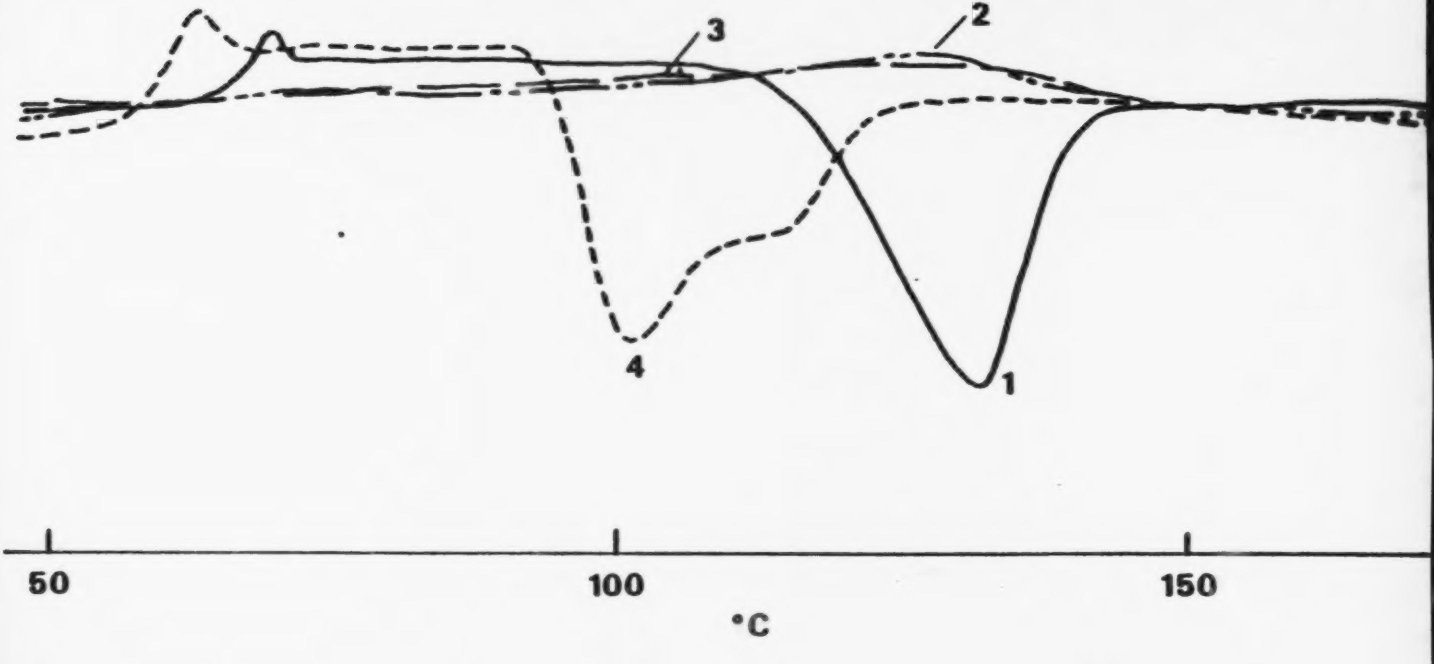

Fig. 13. Differential scanning calorimeter curves for glassy polymer. 1) Unaged; 2) Aged 85 °C, 100% RH, 61 days; 3) Aged 85 °C, 100% RH, 103 days; 4) Aged 55 °C, 100% RH, 103 days.

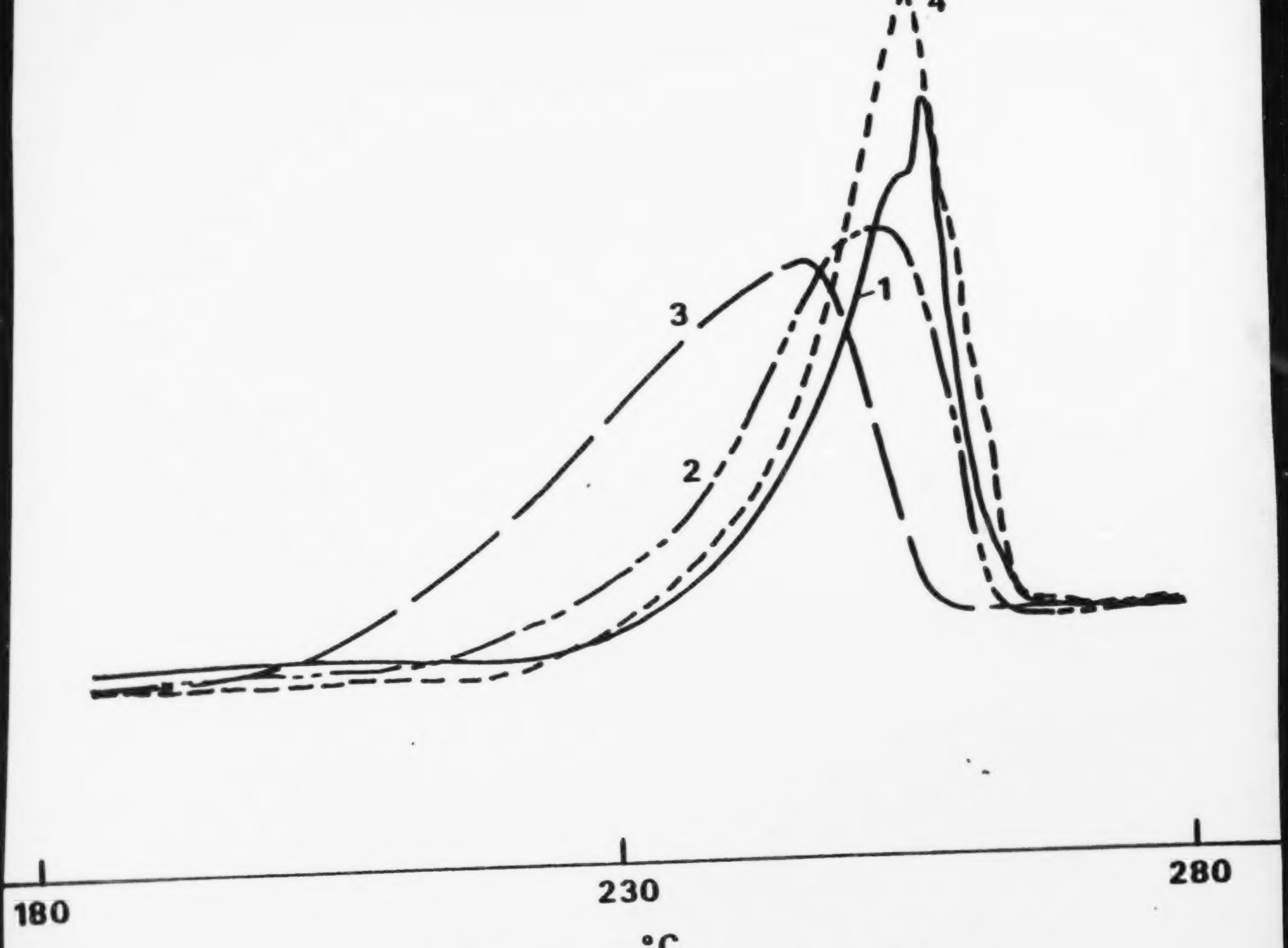

Fig. 14. Differential scanning calorimeter curves for glassy polymer. Same curve designations as in Figure 13.

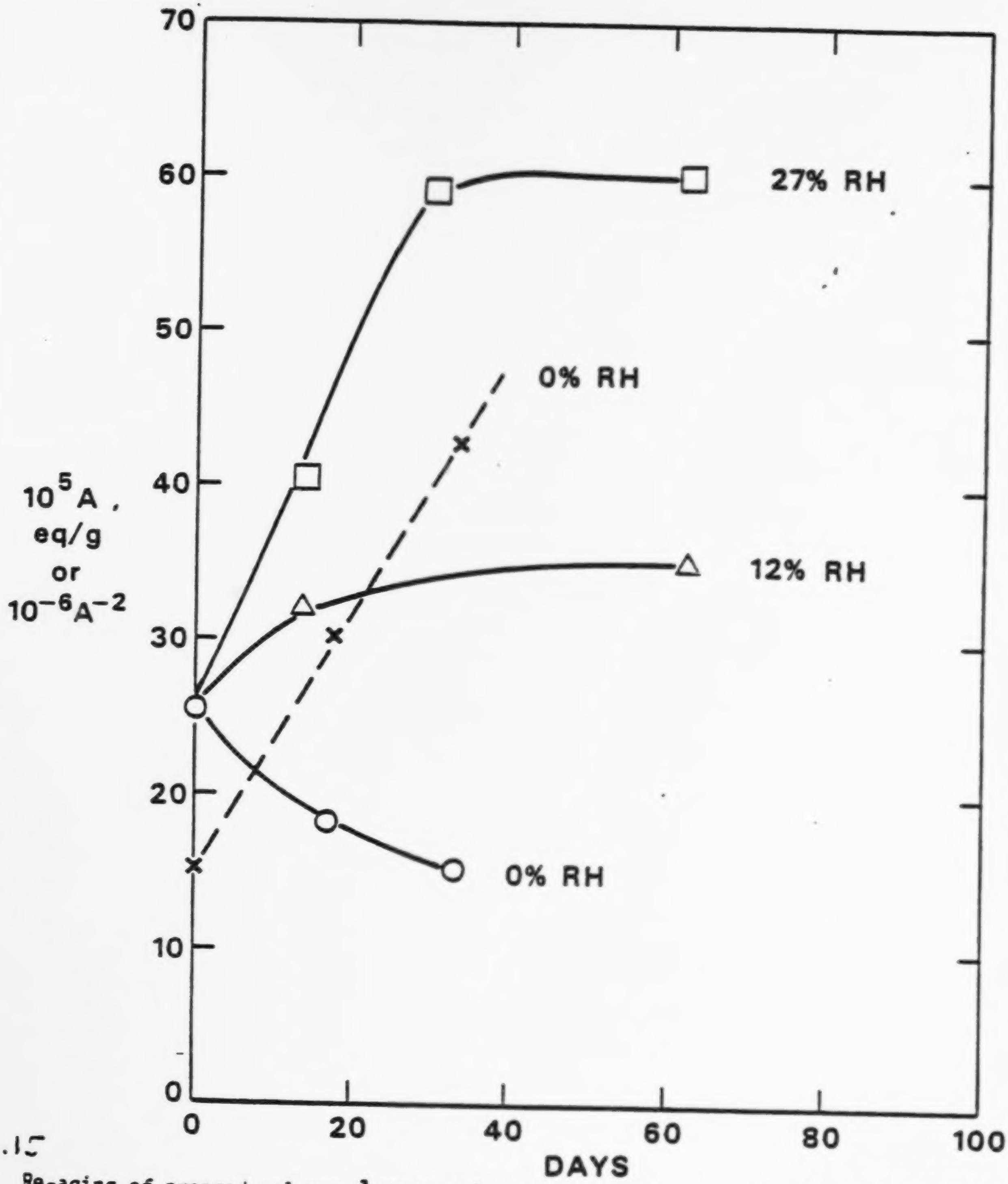

Fig. 15

Re-aging of preaged polycaprolactone polyurethane elastomer. Preaging, 85 °C, 100% RH. Re-aging 85 °C, RH as indicated. [A]: □, 27% RH; Δ, 12% RH; O, 0% RH; X, [A^{-2}] (Dashed line).

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The stability of poly(ethylene terephthalate) is being studied in order to predict its long term behavior as the base of the film and tape used to record archival information. This report contains results of the first year's work. Film base, with and without photographic and other coatings, was aged at several temperatures and humidities. Mechanical and calorimetric properties and molecular weights were measured at intervals. Degradation was relatively rapid at temperatures of 115, 100, and 85°C at 100% relative humidity. The scission rate at 85°C was about 10^{-6} mol scission/g-day and the activatio energy was 113 k J/mol. Rates decreased strongly with relative humidity, becoming negligible in dry air and nitrogen. At 55°C and 100% relative humidity degradation was not significant in 163 days. Samples are seriously embrittled by the introduction of about one scission per molecule--about 10^{-4} mol scission /g. Differential scanning calorimetr showed little change in melting behavior of semicrystalline samples aged at 55 and 85°C. Glassy samples crystallized during aging at 85°C but not at 55°C.

Magnetic tapes based on poly(ethylene terephthatate) usually have a polyester polyurethane binder that holds the magnetic particles. The binder is thought to be more sen sitive to hydrolysis than the tape base. Results obtained with a thermoplastic polyeste polyurethane imply that there may be an equilibrium extent of degradation for any storag condition. It is anticipated that the study will go on for four more years.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

degradation; film base; hydrolysis; photographic film; polyester; poly(ethylene terephthalate); recording media; stability

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PREDICTION OF THE LONG TERM STABILITY OF POLYESTER-BASED RECORDING MEDIA

by

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Abstract

The stability of poly(ethylene terephthalate) is being studied in order to predict its long term behavior as the base for film and magnetic tape. This report contains results of the second year's work. Film base, photographic film, and electrographic film are being aged at several temperatures and relative humidities, RH. Acid contents, mechanical properties, and molecular weight have been measured at intervals. The rate of increase in acid content, k, provides a useful measure of the degradation rate. Data for films aged between 115 and 55 C at 100 % RH obey the equation $\ln k = 39.3 - (14000/T)$, where k is in %/day and T is the absolute temperature. The water content is included in k, which is approximately proportional to RH. Lifetimes of the films appear to be equal to 69.3/k days. Extrapolation to 25 and 20 C gives 400 and 900 years for the lifetime at 100 % RH. A more sensitive analytical method than now used will be required to make useful measurements of acid content at 35 C, even after samples have been aged for five years. Two films have always failed before the others. The short-lived films might well be stored with others, since failure of the former would warn of the approaching failure of the latter.

Magnetic tapes are also being aged, primarily to study the binder that holds the magnetic oxide to the substrate. Binder on five brands of tape that were aged at 60 C became crosslinked at RH of zero and 11 %, changed little at 30 % RH, but degraded at 100 % RH. The binder on tapes aged at 85 C and 100 % RH first degraded severely and then appeared to crosslink slightly. Badly degraded binder was not gummy but was easily detached from the substrate. Model binder aged at 85 C and 100 % RH eventually became brittle.

Key words: degradation; hydrolysis; lifetime; magnetic tape; photographic film; poly(ethylene terephthalate); stability

1.0 Introduction

Data of many kinds are recorded and stored on photographic film and magnetic tape. Both media contain an active element in a dispersing medium bonded to a substrate consisting of poly(ethylene terephthalate), PET. A PET-based electrographic film is now available which can be revised. The lifetime of the PET under common storage conditions is very long but not known. The lifetime of the dispersing medium for the iron oxide particles of magnetic tapes is also uncertain but is expected to be less than that of PET because the medium is based on polyester polyurethane, which is known to be hydrolytically unstable. For these reasons, the National Archives is sponsoring an environmental aging study of PET and magnetic tapes at the National Bureau of Standards. This is the second annual report in what is expected to be a study lasting five years.

The results with PET in the first year were consistent with the literature. Hydrolytic degradation was the most important process. About 100 days aging at 85 C and 100 % relative humidity, RH, made PET weak and brittle and reduced its molecular weight from about 24000 to 12000. Aging for up to about 150 days at 0, 25, and 50 % RH at 85 C and at 100 % RH at 55 and 35 C caused almost negligible changes in tensile strength, elongation, and molecular weight. About one chain scission per molecule or 5×10^{-5} mol scissions per gram brought about embrittlement, but the imprecision in these quantities was about 50 %. Thus, although PET appeared extremely sensitive to changes in molecular weight, such measurements were not a practical way of measuring the very small amounts of degradation necessary to assess changes at 55 and 35 C or those under ambient conditions.

Acid content is another possible measure of degradation, since each hydrolysis reaction generates an acid group when it breaks the polymer chain. We had procured a potentiometric titrator,in order to measure acid content, but had not had an opportunity to use it before the first report.

Polyester polyurethanes were known to be susceptible to hydrolysis, so this was expected to be the reaction that determined tape lifetime. Our own studies with magnetic tape had not been started at the time of writing the first report. It had been reported that the degradation of the polyester polyurethane binder, which holds the magnetic particles, was limited by the equilibrium between hydrolysis and esterification and it was concluded that tapes stored at 18 C and 40 % RH should retain acceptable properties indefinitely because of this [1]. We equilibrated polyesters and two polyester polyurethanes at various RH and concluded that hydrolytic equilibrium did not prevent serious loss of properties [2]. However, tape binder differs from the polymers that we studied in that it is highly crosslinked and so may behave differently.

In the second year of work agings have been continued and additional data of the same kind obtained. Acid content was evaluated as a means of measuring degradation of PET. Commercial magnetic tapes were aged and are being evaluated as in reference [1].

2.0 Experimental

PET samples included coated and uncoated electrographic film, exposed and developed photographic film, and uncoated film base, all commercially available. Most of these materials were provided by the National Archives but we purchased the film base. We were also given amorphous PET. Some of this was crystallized and some was stretched uniaxially without crystallizing it. Experiments with the latter two samples should give us some knowledge of the effect of crystallinity and orientation on hydrolysis.

Samples of PET were aged in closed containers above water or solutions of LiCl at temperatures of 85, 70, 55, and 35 C and RH of 100, 50, and 25 %. At intervals tensile strength and elongation were measured on a tensile testing machine and molecular weight was measured by gel permeation chromatography, as described in the previous report. Other agings were done in boiling water.

Acid content was measured by potentiometric titration with tetrabutyl ammonium hydroxide in ethanol as base. The polymer was dissolved in a mixture of o-cresol and chloroform. The titrator adds increments of base when the rate of change in the voltage has decreased to some preset value. The end point is reached when the difference between the voltages at successive increments first exceeds and then drops below some preset value. The measurement is precise to about 2×10^{-6} mol acid. This method was used because it is being considered as a standard for the PET base of photographic film certified for achival use.

Ten rolls each of six brands of magnetic tape were purchased. Rolls contain 750 feet of tape except for one set of 2000 foot rolls. All tapes are 1/2 inch wide and are certified for 6250 bpi. Tapes were the most expensive that the suppliers offered except for the 2000 foot rolls, for which the more expensive and less expensive grades are both being tested. The tapes are being aged at temperatures of 85, 60, and 37 C and RH of 0, 11, 30, and 100 %.

Model tape binder was made in order to explore effects in the absence of the magnetic particles. A commercial polyester polyurethane was dissolved in tetrahydrofuran. Enough toluene diisocyanate was added to react with each urethane group. The tetrahydrofuran was evaporated and the mixture was heated at 100 C for five days. The resulting crosslinked film was extracted with tetrahydrofuran. The sol content was less than 1 %. Samples were aged at 100, 50, and 25 % RH at 85 C.

Magnetic iron oxide was procurred and added to a tetrahydrofuran solution of the same polyester polyurethane as above. The tetrahydrofuran was vaporized and the sample was aged at 100 % RH and 85 C for 14 days. Dimethyl formamide was added and the iron oxide was removed by centrifugation. The acid content was then determined.

The weight fraction of binder layer on commercial tapes was determined by immersing about 1.6 g of tape in acetone and then scraping the softened binder and associated oxide off the PET substrate. Then the acetone was evaporated and the dried scrapings weighed. The organic component was then burned off and the residue was weighed, giving the amount of iron oxide. The organic content of the binder layer was taken as the difference between these weights. Soluble portions of the tape were determined by uncoiling about 50 feet into a 4 liter beaker. This was extracted with two 750 cm^3 portions of tetrahydrofuran for a total time of 1 hour. The sol fraction was determined by drying and weighing the tape and by evaporating the filtered solvent to dryness and weighing the residue. Final weighings were made after 60 hours of evacuation. The tapes are quite hygroscopic and weighings were made in closed containers.

The adhesion of the binder layer was tested by applying 3/8 inch-wide sticky tape to the binder layer of unextracted tape and peeling it off in a testing machine. The force required went through an initial maximum and then decreased and became approximately constant during most of the peel. The latter force was taken as the peel strength. The noise level during the peel was about 1/4 to 1/2 as large as the value taken, so the peel strength is not very precisely known. Despite this it should be significant because it varies widely between brands of tape and even between rolls of the same brand, in the case of one brand. Peel strengths on other brands did not change from roll to roll.

Generally, five 50-foot lengths of a single tape were aged in a closed jar at each temperature and humidity mentioned above. Solutions saturated with LiCl and $CaCl_2$ gave 11 and 30 % RH. Molecular Sieves were used to get 0 % RH. Individual lengths of tape were removed at intervals and the sol content and peel strength were measured as described above. Tensile strength and elongation were also measured.

3.0 Results

3.1 PET.

3.1.1 Preliminary Acid Measurements. The American National Standards Institute Vesicular / Toned Image Task Force ran a round robin using two methods of measuring acid content in PET. We participated in this in order to gain experience with the titrator and the technique. Five samples of PET were analyzed in duplicate by the two methods. All laboratories preferred the method described in the section above. The range of acid contents of the samples was 0.29 to 0.50 X $^{-4}$ equiv./g and our values were within that range. A second purpose of the round robin was to measure the effect of the accelerated aging described in ANSI PH1.41-1981 on acid content. All laboratorise found no significant effect.

Our laboratory offered to try to find conditions that would offer a more meaningful accelerated aging test. Samples of PET polymers were aged in boiling water and portions were removed at intervals. Tensile strength, TS, elongation, E, and acid content, [A], were measured after the aging was ended. The polymers used were the film base that we used previously and the samples from the round robin that had the highest and lowest acid contents, designated here as E and F. The results obtained are listed in Table I. Values are generally means of two or more determinations.

Acid content increases with aging time. After 17 days the differences between acid contents of the three samples had increased by factors of between three and four. Tensile strength and elongation decrease with aging. About one third of the film base removed as one piece at 14 days broke when it was creased. The remainder, also one piece, did not break when creased. Acid content, tensile strength, and elongation all indicate significant differences between the two portions. The reason for this behavior is unknown.

Titrations are believed reproducible to about 2 X 10^{-6} equiv. acid. They were done in duplicate except for sample E at 17 days. The average difference between duplicate determinations was 2.2 X 10^{-6} equiv. (2.4 X 10^{-6} equiv. std. dev.). Portions of polymer used usually contained about 10^{-4} equiv. of acid, so the relative imprecision is about two percent.

Hydrolysis of PET is catalyzed by acid and is autocatalytic because of the acid generated [3]. The reaction is:

$$H_2O + -(C_6H_4CO_2C_2H_4O_2C)- \xrightarrow[A]{k} -C_6H_4CO_2H + HOC_2H_4O_2C- \qquad (1)$$

Here A represents an acid group and k the rate constant. The water and ester contents change little during the portion of reaction of interest so they can be included in the rate constant. The differential equation connecting [A] and time, t, is $(d[A]/dt) = k\,[A]$, which integrates to $\ln([A]/[A_0]) = kt$, where the subscript indicates the initial concentration. Fig 1 is a plot of $\ln([A]/[A_0])$ versus time. The slope is approximately the same for the three polymers, 8.0 % / day. This represents the rate of increase in acid content.

An initially greater acid content results in greater increases in acid content during aging. Thus the technique makes differences between polymers more obvious. From these data it appears that polymer F originally had a higher acid content than E.

Elongation of film base changes very suddenly between 10 and 14 days aging. One might think of using a ten day aging period in boiling water as an accelerated test and making the criterion of failure be that the acid content not exceed 10^{-4}equiv/g at the end of that period.

3.1.2 PET at 85 C Acid content, number average molecular weight (M_n), tensile strength, and elongation for the unaged PET materials are in Table II. The initial range of acid content is 0.31 to 0.48 X 10^{-4} equiv/g. Aging at 85 C at 100, 50, and 25 % RH increases acid content and reduces tensile strength and elongation, eventually embrittling the material. Data in Table III show these effects for the film base. Samples of aged polymers were small and the imprecision in [A] is about 10 %. "Y" or "N" in the column headed "Crease" indicates whether or not the samples could be creased without breaking. Elongation must be very low for failure to occur since samples could be creased that had as little as 5 % elongation.

Microfilms A and B, encapsulating film, and coated electrographic film D behaved about the same as film base. Uncoated electrographic film C became brittle much earlier. It failed the crease test at 61 days at 100 % RH, 81 days at 50 % RH, and 341 days at 25 % RH. Coated electrographic film C failed at intermediate times: 81, 148,and 650 days at 100, 50, and 25 % RH, respectively. It is uncertain whether the slightly higher initial acid content of the C films caused their early failure, because there were also initial differences in elongation and heat of fusion, commented on in the the first report. Presumably these differences are due to variations in orientation and crystallinity, which could affect the behavior in hostile environments.

Changes in M_n offer an alternative to acid measurements as a means of calculating the rate constant, k. Each hydrolytic scission increases the number of acid groups and the number of polymer molecules by one, as shown in reaction 1. Thus the change in the concentration of acid groups, $[A] - [A_0]$, is the same as the change in the concentration of polymer molecules, $\Delta(M_n^{-1})$, so that $[A] = [A_0] + \Delta(M_n^{-1})$ and $\ln\{([A_0] + \Delta(M_n^{-1}))/[A_0]\} = kt$. Values of k were calculated from this expression and from $\ln[[A]/[A_0] = kt$ by assuming a linear variation of the logarithmic quantities with time and using the method of least squares to calculate the slopes, designated k_M and k_A, respectively. They are listed in Table IV. The imprecision indicated is the standard error; where none is given only two points were used to calculate the slope. The averages of the values in each column are listed at the bottom of the table with their standard deviations. Neither k seems to depend on the particular film used but values of k_A are somewhat larger than k_M. Probably this is due to some systematic error in the molecular weights, which were measured by GPC. For practical purposes k_M and k_A are treated as the same quantity, k.

3.1.3 PET at 115, 70, 55, and 35 C at 100 %RH A sample left from last year that was aged for 13 days at 115 C and 100 % RH in a sealed glass tube has an acid content of 7.35 X $^{-4}$ equiv/g. The value of k_A is 22.6 %/day.

Data obtained with film base and microfilm B at 70 C are in Table V. The acid contents of these samples have not yet been determined. Values of k_M are 0.25 and 0.19 %/day for film base and microfilm B, respectively.

Most of the samples aged at 55 C and 100 %RH have shown no significant changes in tensile strength, elongation, or molecular weight in almost two years. However, the elongation of the film base of uncoated C was only 63 %, down significantly from 180%. There has also been a significant change in the acid number of the film base. Duplicate determinations on samples which each had about 0.8 X 10^{-4} equiv. of acid gave acid contents of 0.44 and 0.43 X 10^{-4} equiv/g after being aged for 586 days. The average value of k_A is 0.037 %/ day.

No detectable change occurred in the PET in samples aged for two years at 35 C and 100 %RH but the coatings on these films have deteriorated even at 35 C and 25 % RH. The gelatin layer of the microfilms has become sticky and even disappeared immediately above the LiCl solution. Electrographic films D and coated C have discolored. We have no samples of these with images and so can not assess the effect on the legibility.

3.1.4 Lifetime of PET Fig 2 is an Arrhenius plot of the rate constants at 100 % RH. The least squares line is shown. The slope of this line gives an activation energy of 117 kJ/mol or 28 kcal/mol. This value agrees well with 27 kcal/mol that we gave last year and also with the value 29 kcal/mol found by McMahon et al. [4].

The glass transition temperature of PET is about 70 C, so finding that the rate at 55 C falls on the same Arrhenius line as rates above the glass temperature implies that it is valid to extrapolate to still lower temperatures. This was done to give rates at 100 % RH at 35, 25, and 20 C. The lifetime, t_L, can be estimated from these rates as follows. Data in Tables I and III indicate that the acid content approximately doubles before the tensile strength and elongation deteriorate seriously. Consequently, the lifetime was taken as (ln 2)/k, where k is the fractional rate of change in the acid content. Values of t_L at the three temperatures above are about 90, 400, and 900 years. Data in Table IV indicate that lifetimes at 50 % RH at the same temperatures should be more than twice as long. The lifetimes agree with those estimated by Adelstein and Mc Crea [5].

It is gratifying that these estimated times are so long but it should be noted that the result is greatly dependent on the value at 55 C. The acid content at 55 C should double before this study ends, which will permit more accurate measurement of k. It is desirable to get a measurement at 35 C to reduce the extrapolation range.The change in acid content at 35 C should be about 2 % after five years, which will be barely significant with the current methods.

3.1.5 Future plans with PET The agings will be continued and the acid content at 55 C will be determined with better precision. It is desirable to measure the acid content with about 10 fold greater precision than now being done, in order to measure k at 35 C. Increasing the sample size would help to some extent, but it is already large and using much more would exhaust even our largest samples fairly quickly. An infrared method has been described [6] that involves exposing PET to sulfur tetrafluoride. This converts acid groups to acid flouride groups. These absorb far enough from the ester carbonyl absorption to appear as a separate peak. We intend to test this method using aged samples with known amounts of acid.

Oriented amorphous PET is being aged at 70 C and 100 % RH. Unfortunately, aging it at 85 C causes crystallization, which we wish to avoid. Crystalline PET is also being aged. Results from both samples should be available in about one year. They should give information about the relative importance of amorphous and crystalline regions in the degradation process.

3.2 Magnetic Tapes

3.2.1 **Background** Magnetic tapes consist of Fe_2O_3 particles dispersed in a polyester polyurethane-based binder that is bonded to a PET substrate. Conversations with manufacturers who supply products to tape producers indicate that magnetic tapes are made in the following manner. The oxide is coated with a wetting agent, which may be butoxy ethyl stearate or ethyl stearate. A commercial polyester polyurethane is dissolved in tetrahydrofuran. To this are added the oxide and a multifunctional polymeric isocyanate The suspension is applied to the substrate and the combination is then heated to remove solvent and bring about reaction between the urethane and isocyanate groups to form allophanate linkages:

$$-NCO + -NHCO_2- \longrightarrow -NHCO\overset{|}{N}CO_2- \qquad (2)$$

Catalysts are used to speed up the reaction and a coupling compound may be used to make the binder adhere to the substrate. The binder is highly crosslinked because of the allophanate reaction.

There are about 10 aliphatic ester linkages between urethane links in the original polyester polyurethane. These are more subject to hydrolysis than the aromatic ester linkages of PET and most polyester polyurethanes degrade to soft non-rubbery materials in 10-15 days at 85 C and 100 % RH. The hydrolysis obeys the same kinetic equations as the PET hydrolysis [7]. Lifetimes under ambient conditions are much longer, but in warm moist environments polyester polyurethanes have been known to fail in three years.

Magnetic tapes usually last longer than this, perhaps because their environment is not very humid, but another factor seems to be involved. Cuddihy [8] showed that the acetone-extractable fraction of tape binder on tapes aged for up to 85 days at 36-75 C increased at 100 and 30 % RH but decreased at 11 and 0 % RH. He attributed the decrease to esterification, the reverse of reaction (1), and predicted that tapes could be stable indefinitely because of the equilibrium between esterification and hydrolysis. Decreasing the temperature at constant RH increased the esterification tendency, leading Bertram and Cuddihy to recommend 18 C and 40 % RH as ideal storage conditions [1]. They found that tapes could be used without problems if the content of extractable was less than twice the initial value. Working with soluble polyesters and polyester polyurethanes, we found that acid content at 35 C and 25 %RH changed in 300 days from 3.5 to 3.8 X 10^{-4} equiv/g, implying that equilibrium was near or that the time to reach equilibrium was very long [2]. The molecular weight should equal $[A]^{-1}$ g/mol so it could be as low as 2700. Speculations were made that the high cross link density of tape binder encouraged esterification or caused the binder to remain as gel despite having many chain ends [2].

Cuddihy worked with only about 1.5 g of tape in his samples and the weight fraction of acetone extractable material ranged from 10 to 80 mg. His data are for one unidentified brand of tape although he notes that other tapes behaved similarly. The use of acetone as an extractant raised the possibility that molecular weight limited the weight of extractables, because acetone does not completely dissolve the polyester polyurethane used to make tape binder. Our measurements with this polyester polyurethane gave 7000 and 28000 for the molecular weights of the acetone-soluble portion and the whole polymer, respectively. For these reasons it was decided to repeat the Cuddihy procedures using tetrahydrofuran to extract 10-15 g samples of several brands of tape.

3.2.2 Initial Tape Characteristics Table VI lists the weight percentages of the binder layer (oxide plus associated binder and other organic components) and the sol content of each unaged brand of tape. The peel strength is also given. The last two columns give the weight percentage of organic material in the binder layer and the portion of this organic material that is extractable. These two quantities are dependent on the weight of iron oxides and may be inaccurate if the oxides changed when the organic component was burned off. Tape 1 has a back coat that contains carbon. Soluble components of this are included as "Sol" and it was assumed that the coating was 50 % carbon in calculating the value in the last column. Tape 3 contained an acetone-soluble white crystalline material that appeared as a residue surrounding the fragments of binder layer when the acetone had evaporated. This was not observed with the other tapes. The Sol was determined from the weight loss of the tape except with tape 4. The binder layer fell off this tape as soon as it was immersed in tetrahydrofuran so the sol content was determined by filtering the mixture and evaporating the solvent.

Double listings under Sol give results of duplicate determinations and give some feeling for the imprecision of the measurements. These duplicates were averaged in calculating the sol as a percentage of the organic component of the binder layer. The amounts of sol and the peel strengths very widely from tape to tape. A greater then sign means that the binder layer did not peel off. Peel strength of tape 5 varied from reel to reel, accounting for the wide limits listed. Portions taken at 400 foot intervals on one reel each of strongly adhering and weakly adhering binder revealed no samples from which binder was stripped from the former reel and no stripping force greater than 40 N/m from the latter reel. Measurements have not yet been performed on tape 6, which is the more expensive of the two grades of tape purchased from one supplier. Tape 5 is the less expensive of these two grades. The supplier of tapes 5 and 6 is not a manufacturer, but has tapes made to his specifications and sells them under his own label. The other tapes bear manufacturer's labels and were purchased from authorized retailers.

3.2.3 Tapes at 85 C and 100 % RH Table VII gives results obtained by aging four brands of tape at 85 C and 100 % RH. Tensile strength and elongation were seriously affected after 46 days. Tapes 1 and 5 broke during handling. Acid contents of these tapes will be determined. The sol content goes through a maximum. The peel strengths were low but were not measured because the tapes were rather brittle. None of the binders became soft or gummy during aging. Instead they tended to flake off, and it was necessary to determine sol fractions by evaporating the tetrahydrofuran. Ordinary polyester polyurethanes would be very soft after 46 days under these conditions.

3.2.4 Tapes at 60 C Table VIII shows the effect of aging the tapes for 85 days at 60 C at 0, 11, 30, and 100 % RH. Values for the unaged tapes are included. The sol contents show the same trend as Cuddihy's data: decreased sol at 0 and 11 %RH and increased sol at 100 % RH. Aging at 30 % RH caused little change in the sol content. Peel strength decreased to about 2/3 of its original value in tape 1 and to 1/10 of its original value in the other tapes at 100 % RH. Aging at lower RH caused smaller changes in peel strength. Significant loss of peel strength occurs at 30 % RH, which might limit tape lifetime. None of the binders appears to have softened during aging.

Peel strengths have been measured at other times during these agings. Most of the loss of strength occurs in the first 40 days.

Tensile strength and elongation have not yet changed significantly in any sample at 60 C.

3.2.5 Model Studies The model tape binder did not soften when aged for two months at 85 C at any RH. Instead samples became stiffer and that aged at 100 % RH is actually brittle. These results appear consistent with the observation that binder layer on magnetic tapes aged at 60 and 85 C did not soften. It may be that there are reactions in addition to hydrolysis and esterification and that some currently unknown reaction brings about crosslinking.

The sample of the polyester polyurethane that was mixed with magnetic iron oxide and aged at 85 C and 100 % RH formed acid faster than polyester polyurethane without the iron oxide. Thus it appears that tape binder ought to be destabilized by the heavy loading of iron oxide.

3.2.6 Future plans with magnetic tapes The agings will be continued. Results from the agings at 37 C will be obtained within a few months. It is planned to put data on tapes from each supplier and store them at 50 and 100 % RH at 20-25 C. These will be read at intervals. More experiments are planned with model binder polymers.

4.0 Discussion

The findings with PET indicate that the material should be quite stable at ambient conditions provided that the process by which PET is made and the rather specific combination of orientation and crystallinity now given the polymer are not changed. If changes were to be made, some knowledge of their effect on stability would be useful.

One could make use of the fact that coated and uncoated films C lose tensile strength and elongation faster than the other materials. Samples of film C could be stored under the same conditions as films used to store archival information. Our results indicate that uncoated C would fail first, followed by coated C. There would be ample time before the failure of the films containing archival information for it to be copied on fresh material.

The changes in the coatings under relatively mild conditions are somewhat disturbing. The films are exposed to laboratory light for about 1/3 of the time. Deterioration of the coatings is usually worst immediately above the liquid interface. Photographic gelatin has been used for a very long time and it was our impression that it would be stable at 35 C at low RH.

The studies with tapes are not far enough along for us to have come to any firm conclusions. However, we suspect that other reactions than hydrolysis and esterification play a significant part in the process.

5.0 Summary

PET has been aged for about two years. Samples aged at 100 % RH at 85 and 70 C deteriorated relatively rapidly. One particularly labile sample shows loss of tensile strength and elongation after aging at 55 C and 100% RH. Lower RH results in much slower degradation but all PET samples at 25 % RH and 85 C lost most of their tensile strength and elongation within two years. Tensile strength and elongation decreased as acid content increased. An increase in acid content of about 0.4×10^{-4} equiv/g from an initial value of about 0.3×10^{-4} can be tolerated. PET became quite brittle when the acid content exceeded 10^{-4} equiv/g. The relation between acid content and time is $[A] = [A_0] \exp kt$. The primary difficulty with using acid content to monitor PET degradation is that the required sample size is inconveniently large. An effort is being made to address this problem.

Various magnetic tapes are being aged at different temperatures and humidities. The tapes are rather different initially, in so far as extractables and peel strength are concerned. Sol contents increase at 100 % RH but decrease at low RH. The binder layer behaves differently from the polyester polyurethane from which it is derived since the former does not seem to soften during aging. The reasons for the difference are unknown.

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TABLE I

Acid Content, Tensile Strength, and Elongation at Break of PET Aged in Boiling Water

Time Days	[A] 10^{4} equiv/g	TS MPa[1]	E %
	Film Base (4 mil thick)		
0	0.36	215	142
3	0.45	192	130
5.9	0.55	179	135
9.7	0.73	150	103
14.0	1.05	116	40
14.0	1.15	71	2
17.0	1.41	Weak	Brittle
	E (7 mil thick)		
0	0.29	162	90
3	0.36	173	113
5.9	0.45	171	97
17	1.13	95	4
	F (4 mil thick)		
0	0.50	--	--
17	1.84	weak	brittle

[1] 1 MPa = 145 PSI.

Table II

Properties of Unaged PET[1]

	10^{-4} [A] equiv/g	10^{-4} M_n g/mol	TS MPa	E %
Film Base	0.35	1.77	204[2]	144
Microfilm A	0.31	2.15	200	126
Microfilm B	0.32	1.69	193	122
Encapsulating Film	0.37	1.59	177	80
Uncoated Electrographic Film C	0.41	1.44	116	185
Coated Electrographic Film C	0.48	1.54	167	105
Coated Electrographic Film D	0.34	1.68	201	99

[1] 4 mil films except D which is 4.8 mil.

[2] 1 MPa = 145 PSI.

TABLE III

PET Film Base at 85 C

Time Days	RH %	10^4[A] equiv/g	10^{-4} M_n g/mol	$10^5\Delta(M_n)^{-1}$ mol/g	TS MPa	E %	Crease Y/N
Unaged	-	0.35	1.77	0	204	144	Y
61	100		1.15	3.0	170	113	Y
76	100	0.64	1.13	3.2			Y
81	100	0.85	1.07	3.7	108	18	Y
97	100	1.25	0.85	6.1	114	5	Y
108	100		0.80	6.9	weak	brittle	N
178	100	5.05	0.55	12.5	weak	brittle	N
97	50		1.19	2.7	158	80	Y
146	50		1.41	1.4	150	100	Y
340	50	1.66	0.68	9.1	weak	brittle	N
154	25		1.77	0	190	142	Y
341	25		1.34	1.8	155	107	Y
650	25				136	78	Y

Table IV. HYDROLYSIS RATE CONSTANTS IN PET FROM ACID CONTENT (k_A) and MOLECULAR WEIGHT (k_M) at 85 °C

Units of k_A and k_M are %/day

Polymer	100% RH		50% RH		25% RH
	k_A	k_M	k_A	k_M	k_M
Film Base	1.49 ±0.09	0.92 ±0.13	0.45	0.36 ±0.08	0.12
Microfilm A	1.27	1.14 ±0.08	0.47	0.41 ±0.02	0.12 ±0.07
Microfilm B	1.33	1.09 ±0.01	0.48	0.22 ±0.01	0.20 ±0.10
Uncoated C	1.80	0.67	0.68	0.29 ±0.07	0.16 ±0.07
Coated C	1.24	1.14 ±0.12		0.39 ±0.04	0.14 ±0.01
Coated D	1.51 ±0.06	0.84 ±0.30	0.56	0.28 ±0.10	0.21 ±0.03
Encap. Film	1.02 ±0.27	1.10 ±0.08	0.50	0.38 ±0.04	
Average	1.38 ± .25	1.02 ±0.19	0.52 ±0.09	0.33 ±0.07	0.16 ±0.04

Table V

PET at 70 C and 100% RH

Material	Time/days	$10^{-4}M_n$/g/mol	TS/MPa	E/%
Film Base	0	1.77	204	144
	136	1.41	183	124
	312		117	39
Microfilm B	0	1.69	193	122
	136	1.46	132	75
	312		110	23
(1)	136	1.46	131	65
(1)	312		128	56

(1) Microfilm B aged after removal of the gelatin layer.

Table VI

Characteristics of Unaged Magnetic Tape

Tape	Binder Layer (BL) wt%	Sol Content wt%	Peel Strength[1] N/m	Organic in BL wt%	Sol in Org BL wt%
1	20[2]	0.8, 0.9	325	30[3]	9.5[4]
2	23	1.4	> 800	24	25
3	32	2.1, 2.6	150	25	30
4	24	4.8	> 800	29	69
5	28	0.7, 0.6	35->450	26	9.7

[1] 1N/m = 1.02 g/cm

[2] Not including the back coat with carbon black that is 6% of the tape weight

[3] Oxide binder only

[4] Assuming half the back coat is carbon

Table VII

Effect of Aging Magnetic Tape at

85 C and 100% RH

Time Days	TS MPa	E %	Sol %	Sol in Org BL
		Tape 1		
0	230	139	0.8	9.5
18			4.7	56
46	130	5	4.3	51
		Tape 2		
0	290	118	1.4	25
18			3.0	55
46	143	40	2.4	44
		Tape 3		
0	230	103	2.4	30
18			2.4	30
46	130	32	1.8	23
		Tape 5		
0	220	130	0.7	9.7
18			5.0	69
46	115	4	4.1	57

Table VIII

Effect of Aging Magnetic Tapes at 60 °C for 85 Days

R.H. %	Sol wt%	Sol in Org BL wt%	Peel Strength(1) N/m
		Tape 1	
Unaged	0.8	9.5	325
0	0.5	6.0	350
11	0.6	7.1	
30	0.5	6.0	250
100	4.6	55	200
		Tape 2	
Unaged	1.4	25	>800
0	0.8	15	>600
11	1.0	18	>650
30	1.3	24	100
100	2.7	49	50
		Tape 3	
Unaged	2.4	30	150
0	1.4	18	140
11	1.8	23	
30	2.3	29	60
100	5.4	68	15
		Tape 4	
Unaged	4.8	68	>800
0	4.0	56	>700
11	3.5	49	
30	4.4	62	>750
100	5.0	77	25
		Tape 5	
Unaged	0.7	9.7	>450
0	0.4	5.5	>500
11	0.3	4.2	
30	0.7	9.7	>400
100	5.3	74	12

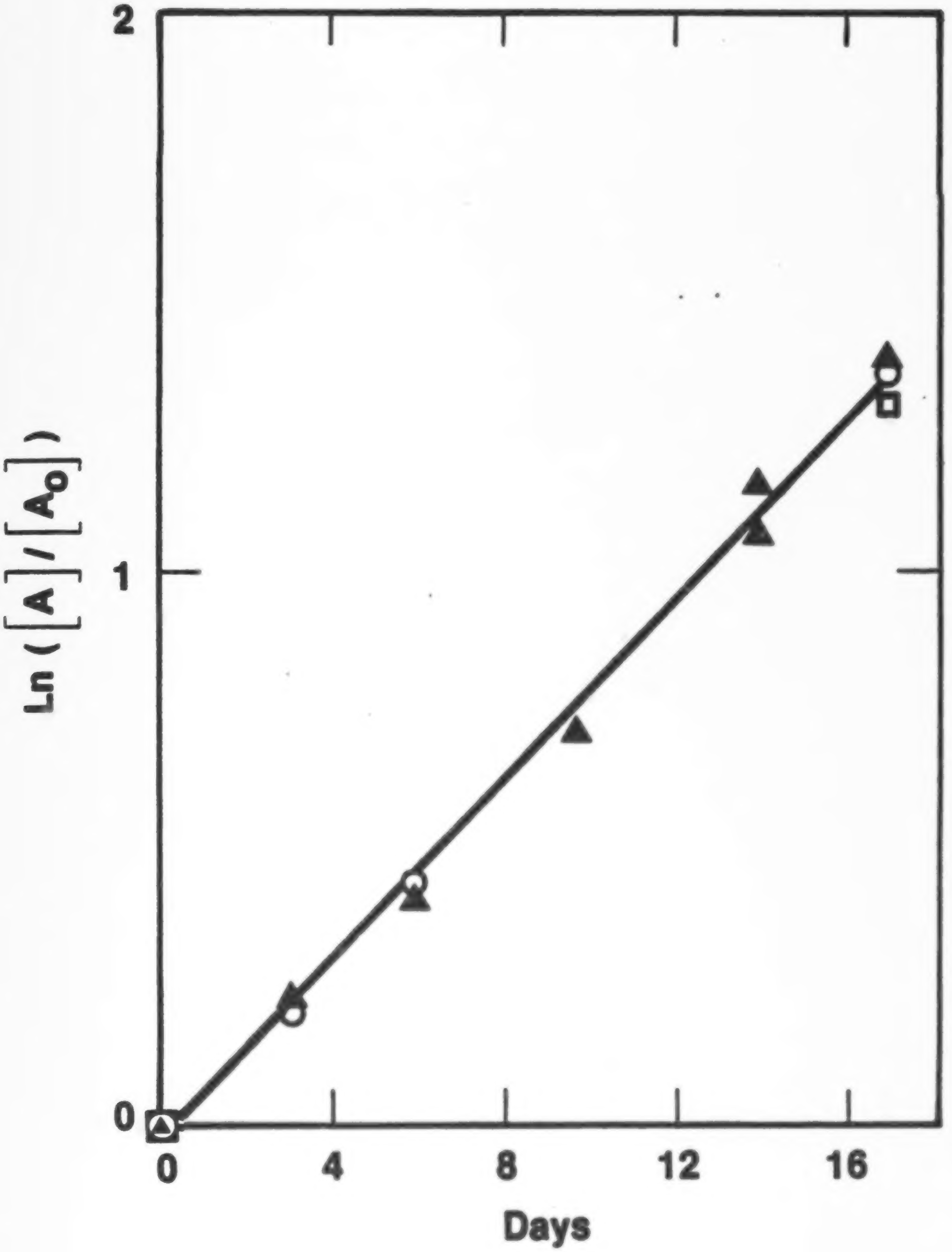

Fig. 1 Ln ([A] / [A$_o$]) vs Aging time in boiling water.
▲, Film base; ○, polymer E; □, polymer F;
—, Ln ([A] / [A]) = 0.080 t - 0.017

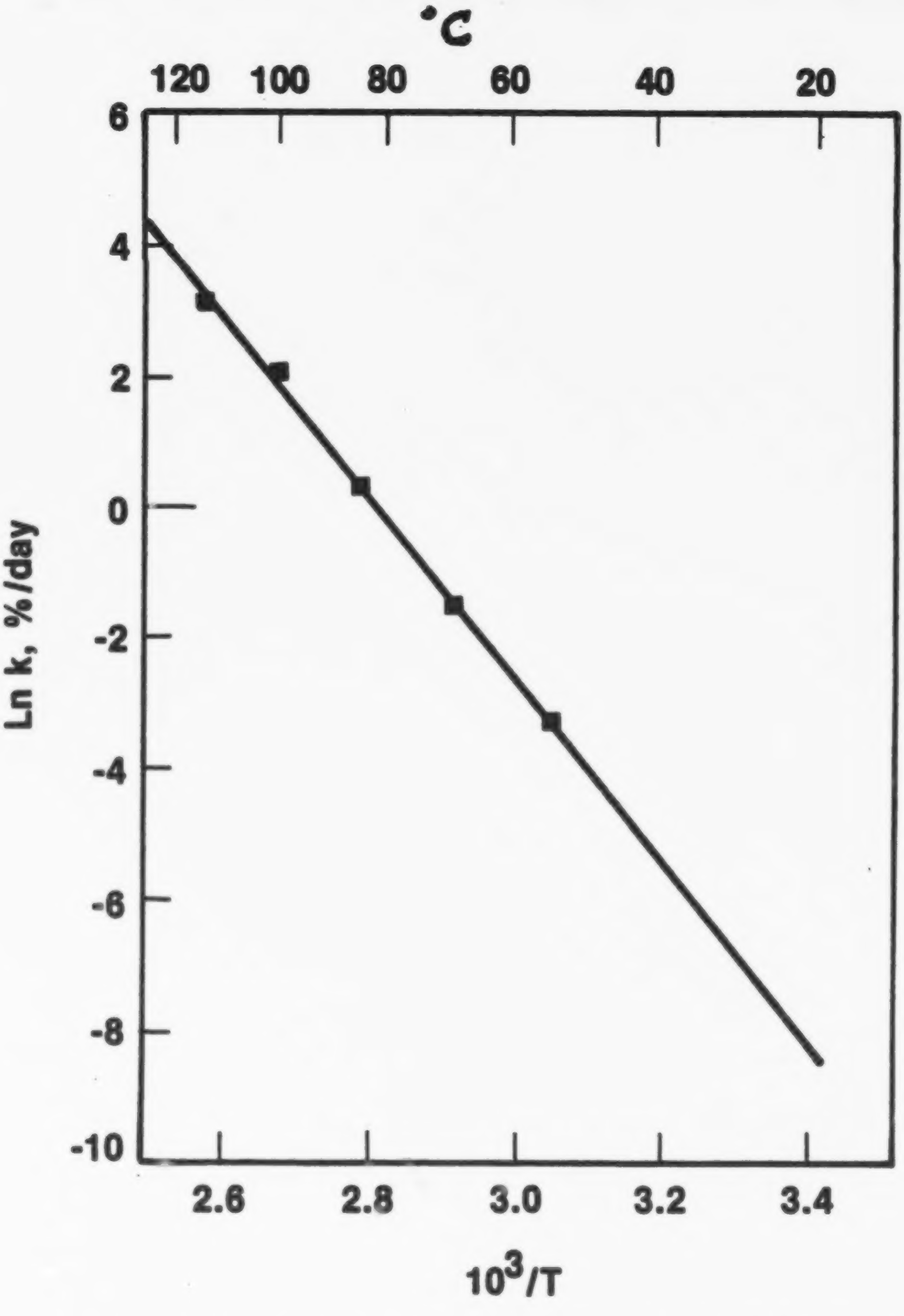

Fig. 2 Arrhenius Plot for PET at 100% RH. k_A was used when it was available; otherwise, k_M was used. —, Ln k=- (14000/T) +39.3

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D.W. Brown, R.E. Lowry, L.E. Smith

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

The stability of poly(ethylene terephthalate) is being studied in order to predict its long term behavior as the base for film and magnetic tape. This report contains results of the second year's work. Film base, photographic film, and electrographic film are being aged at several temperatures and relative humidities, RH. Acid contents, mechanical properties, and molecular weight have been measured at intervals. The rate of increase in acid content, k, provides a useful measure of the degradation rate. Data for films aged between 115 and 55 C at 100 % RH obey the equation $\ln k = 39.3 - (14000/T)$, where k is in %/day and T is the absolute temperature. The water content is included in k, which is approximately proportional to RH. Lifetimes of the films appear to be equal to 69.3/k days. Extrapolation to 25 and 20 C gives 400 and 900 years for the lifetime at 100 % RH. A more sensitive analytical method than now used will be required to make useful measurements of acid content at 35 C, even after samples have been aged for five years. Two films have always failed before the others. The short-lived films might well be stored with others, since failure of the former would warn of the approaching failure of the latter.

Magnetic tapes are also being aged, primarily to study the binder that holds the magnetic oxide to the substrate. Binder on five brands of tape that were aged at 60 C became crosslinked at RH of zero and 11 %, changed little at 30 % RH, but degraded at 100 % RH. The binder on tapes aged at 85 C and 100 % RH first degraded severely and then appeared to crosslink slightly. Badly degraded binder was not gummy but was easily detached from the substrate. Model binder aged at 85 C and 100 % RH eventually became brittle.

Key words: degradation; hydrolysis; lifetime; magnetic tape; photographic film; poly(ethylene terephthalate); stability

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PREDICTION OF THE LONG TERM STABILITY OF POLYESTER-BASED RECORDING MEDIA

by

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Abstract

Aging studies with poly(ethylene terephthalate) film base indicate the lifetime is equal to about 1000 years if the material is stored at 20-25°C and 50% relative humidity. Concentration changes of acid and alcohol groups that occur as a result of aging have been measured by infrared analysis. Rate constants calculated by this method agree reasonably well with those calculated from acid contents determined by titration.

Crosslinked polyester polyurethanes were prepared as models of the binder of magnetic tape. Aging studies with these materials indicate that they hydrolyze more slowly than ordinary polyester polyurethanes. Samples aged at 85°C at 100, 50, and 25% relative humidity eventually deteriorated greatly in a physical sense.

Magnetic tapes were aged and measurements made of the sol content of the binder and its adhesion to the polyester base. The latter quantity appears to be a more valuable indicator of tape condition than sol content. Values of binder adhesion of six brands of magnetic tape initially varied between 800 and 35 N/m (or g/cm). Binder adhesion in aged tapes was less the higher the temperature and humidity of aging. A tape transport had difficulty processing tape with values of binder adhesion as low as 10 N/m. There was no problem at 35 N/m. It is anticipated that the lifetime of magnetic tapes can be predicted by measurements of binder adhesion.

1.0 Introduction

A five-year environmental aging study aimed at establishing the lifetimes of magnetic tapes and the poly(ethylene terephthalate) (PET) base of photographic and electrographic film is being sponsored at the National Bureau of Standards by the National Archives. This is the third report on this work.

Data of many kinds are recorded and stored on photographic film and magnetic tape. Both media contain an active element in a dispersing medium bonded to a substrate of PET. Electrographic film also has a PET base. The lifetime of PET under mild storage conditions is very long but unknown. The iron oxide of magnetic tape is dispersed in polyester polyurethane, a material known to be hydrolytically unstable. Consequently, there is concern about the keeping qualities of film base and oxide binder.

Earlier results in this study agreed with previous work in that hydrolysis appeared to be the most important degradation process. The chemical reaction in both PET and polyurethane is hydrolysis of the ester linkage:

$$H_2O + -CO_2- \xrightarrow{k} -OH + -CO_2H \qquad (1)$$

The products of this reaction are an acid and an alcohol; in addition, the polymer chain is broken leading to a reduction in the molecular weight. The previous report showed that the increase in the acid content of PET was approximately equal to the increase in the number of polymer molecules, consistent with reaction 1 being the only scission process. The same result had been found earlier with polyester polyurethanes[1].

Reaction 1 is catalyzed by the acid formed so the hydrolysis rate accelerates exponentially at the small extents of reaction sufficient to seriously reduce the mechanical properties. Applicable equations are:

$$[A] = [A_0] \exp(kt) \qquad (2)$$

$$1/M - 1/M_0 = [A_0](e^{kt} - 1) \qquad (3)$$

Here [A], k, t, and M are acid content, rate constant, time, and molecular weight, respectively. Subscripts indicate use of initial values. The rate constant, k, is pseudo first order because the ester and water concentrations do not change significantly. Physically, k is the fractional rate of increase in the acid content. Values of k are approximately proportional to the relative humidity, RH. Units used for [A] are mol or eq acid/g polymer; these are equal quantities. The quantity $(1/M - 1/M_0)$ represents the mol scissions/g polymer.

The rate constant was calculated from rearranged forms of Eq. 2 and 3, $k=[\ln([A]/[A_0])]/t$ and $k=(\ln[(M^{-1}-M_0^{-1}+[A_0])/[A_0]])/t$, respectively. Values were obtained with PET at temperatures between 115 and 55°C at 100% RH and at 85°C at 100, 50, and 25% RH. The set at 100% RH followed the Arrhenius equation closely. Correlation of acid content with tensile strength and elongation at break indicated that doubling the acid content left tolerable physical properties in the films but tripling it caused serious embrittlement. Consequently, Eq. 2 was rearranged to give t explicitly and lifetime was assumed to be equal to (100ln 2)/k or 69.3/k days if k is in %/day. Lifetimes obtained by extrapolation of k to 25 and 20°C were 400 and 900 years, respectively, at 100 % RH. Values at 50% RH are twice as long if k is proportional to RH.

The weakest point in the above analysis is the long extrapolation to ambient temperature. Most of the experimental k are at temperatures above the glass temperature of PET. about 70°C. The only value of k at 55°C was based on a value of $[A]/[A_0]$ equal to 1.24. This k was on the Arrhenius line so we extrapolated linearly below the glass temperature. Values of k based on larger $[A]/[A_0]$ and also at lower temperatures are desired to better validate this extrapolation. Changes in [A] are very slow at temperatures of 55 and 35°C. Samples aged at 55°C are expected to double in acid content in five years; acid contents of those aged at 35°C may increase by only two percent.

Work on PET in this reporting period has been limited to accumulating data on samples aged at 70, 55, and 35°C at 25, 50, and 100% RH and developing an infrared analysis based on the increase in concentrations of acid and alcohol groups during hydrolysis.

The polyurethane binder on magnetic tape was expected to obey equations with the same form as those above. Analysis of the reaction is complicated by the large amount of iron oxide suspended in the binder, the presence of lubricants and wetting agents, and the fact that the binder is crosslinked. Additionally, there is evidence that binder becomes more crosslinked at 0 and 15% RH although it degrades at 30 and 100% RH[2]. In the last reporting period we observed this kind of behavior in six kinds of magnetic tape, although our data suggest slow crosslinking even at 30% RH. Cuddihy attributed cross linking to reaction of acid and ester, i.e., the reverse of hydrolysis and predicted that an equilibrium would be reached that would result in more or less permanently stable tape[2]. Later Bertram and Cuddihy settled on 18°C and 40% RH as the ideal condition for storage[3]. However, soluble polyester polyurethanes do not appear to stabilize at molecular weights sufficiently high to have tolerable physical properties even at 15% RH[4]. Thus there is some uncertainty about what is happening to the binder when magnetic tapes are aged at low RH. Additionally, there is the possibility of the binder becoming detached from the PET backing even if it does not degrade. The binding strength did not deteriorate in tape samples aged at low RH but did at 100% RH[2] and it is uncertain at what RH significant loss in binding strength will occur.

In this reporting period magnetic tapes were aged at several temperatures and RH. Sol fraction and binding force between the magnetic layer and the PET base were measured. Portions of aged tape were tested on a tape transport. Model binder was prepared and aged.

2.0 Experimental

PET samples include coated and uncoated electrographic film, exposed and developed photographic film, and uncoated film base. The National Archives provided all but the uncoated film base, which was purchased. Samples were aged at 70, 55, and 35^{o}C at 25, 50, and 100% RH above solutions of lithium chloride. Tensile strength and elongation at break were measured at intervals on a tensile testing machine. Acid content was measured by titration with tetrabutyl ammonium hydroxide. More details about these methods are given in earlier reports.

Model binders with different crosslink densities were prepared by dissolving a commercial polyester polyurethane in tetrahydrofuran, adding the desired amount of toluene diisocyanate, evaporating the solvent, and curing the film at 100^{o}C under nitrogen for one week. Samples of these films were aged at 25, 50, and 100% RH at 85, 60, and 35^{o}C. Infrared spectra were taken and tensile strength and elongation were measured. Swelling ratio was measured by placing 50 mg. samples in 20 cm^3 of tetrahydrofuran for about 60 hours, decanting the solvent, letting residual droplets evaporate, and weighing the swollen polymer in the closed container. Sorbed solvent was removed under vacuum at 100^{o}C to give dry gel. Densities of solvent and dry polymer were used to calculate the volume swelling ratio by assuming volumes were additive. The sol fraction was calculated by subtracting the gel fraction from one. Some films became completely soluble after aging. Acid contents of these were determined by titration in dimethyl formamide with tetrabutyl ammonium hydroxide.

Six kinds of commercial magnetic tapes were aged at 85, 60, and 35^{o}C at 0, 11, 30, and 100% RH. Aged samples were extracted with tetrahydrofuran to measure the sol content. Binder adhesion was measured by applying sticky tape to the binder layer and using a tensile testing machine to separate the binder layer from the PET base. A tape transport was procured and used to write and read data to and from 50 foot lengths of the aged tapes. The program stopped the test after 25 successful write, read cycles or one unsuccessful one. An unsuccessful attempt was recorded only after several trials, as determined by the transport characteristics.

Infrared spectra were obtained in a commercial Fourier Transform Infrared, FTIR, machine. Signals from 1000 scans at 8 cm^{-1} resolution or from 100 scans at 2 cm^{-1} resolution were averaged to give the spectra.

3.0 Results

3.1 PET

3.1.1 Aging at 70,55, and 35°C Table I lists tensile strength,T, elongation at break, E, acid content, and k for several kinds of PET after different amounts of aging at 55°C and 100 % RH. There are small but probably significant changes in tensile strength and elongation in most of the samples. Uncoated electrographic film C lost almost all of its ability to elongate.

The acid contents are based on titrations unless use of FTIR is noted. The latter technique is described below but the method is not in its final form so we have not made measurements on all the films. Acid content has increased significantly for,all samples tested. Values of k were calculated from the listed acid contents. Uncoated electrographic film C appears to have a higher k than the other films. Unaged, this material had a higher crystalline content than the other films in addition to lower tensile strength and higher elongation.

Tensile strength and elongation did not change significantly when samples were aged at 25 and 50% RH at 55°C or at 35°C at 100% RH for three years. Acid contents have not been measured on these samples.

The long term stability of the various coatings is more questionable than the stability of the PET. Coatings on C and D have changed color even at 35°C. Films aged at 55°C have coatings that are more easily detached than before aging. Some of the changes may be due to light or oxidation, the effects of which will be investigated in the coming period. The photographic films lost the emulsion layer, but only within five cm. of the surface of the LiCl solution used to control the humidity. Positive results were obtained when the denuded areas were tested for Cl^-. Apparently there was inadvertent transfer of salt solution to the film. The gelatin of the emulsion layer must have been affected by the salt solution, which has a high ionic strength.

Amorphous PET was aged at 70°C and 100%RH to determine if it accumulated acid at a different rate than semicrystalline commercial films. Unfortunately, it crystallized during aging so we have ended this effort.

3.1.2 Infra red Studies Figures 1 and 2 show FTIR spectra of dry PET between 3800 and 3100 cm^{-1} using 2 and 8 cm^{-1} resolution, respectively. Specimens were three layers of film base each 0.004 in. thick that had been aged in boiling water, as described in the previous report, for the number of days indicated on the plots. Elongation at break and acid content of the film, as measured by titration, are listed in Table II along with differences between the absorbance at 3717 cm^{-1} and absorbances at 3542 and 3256 cm^{-1}.

The FTIR instrument is continually purged with dry air. Sorbed moisture in the films absorbs in the region plotted so spectra changed appreciably for about six hours as the films dried out, but did not change significantly thereafter. There is ample room in the purged space of the instrument for many samples. Opening the purged space briefly to transfer dried samples to and from the sample holder did not noticeably change the spectra. The procedure adopted was to put samples in the purged space the day before they were to be run so that they had more than 16 hours of drying time.

Spectra at both resolutions show increased absorption between about 3600 and 3100 cm^{-1} as the aging time increases. The whole level of absorption seems to increase although a peak at 3542 cm^{-1} becomes more prominent. There are small, regularly spaced peaks in all the spectra that are due to interference between reflections from the front and back of the films. Increasing the resolution sharpens these peaks but does not change the absorption in other ways.

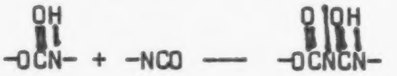
Acid and alcohol groups in PET absorb at 3256 and 3542 cm^{-1}, respectively[5]. Addleman and Zichy have applied infra-red spectroscopy to measure acid and alcohol group concentrations in PET[6]. Their samples had not been artificially aged and acid contents ranged only from 0.49 to 0.59 X 10^{-4} mol/g. Their criterion of dryness was that the sample be more transparent at 3663 than at 3717 cm^{-1}. Our samples dried as described above met this condition. Their method of analysis is considerably more complicated than what we are currently using because they had to allow for differences in crystallinity and orientation, both of which affected the absorption coefficients. Our comparisons are between original and aged material which appear to have the same crystalline content, as measured by differential scanning calorimeter. There are no dimensional changes, which would be expected to occur if orientation changed. It is desirable to orient samples consistently in the instrument beam to minimize effects due to dichroism, but these seem to be only a few per cent in our instrument.

Our method is to use the absorbance at 3717 cm^{-1} as the baseline above which to measure absorbance at 3542 and 3256 cm^{-1}. Table II contains absorbance differences that are means of those found in 8 and 2 $cm.^{-1}$ spectra. Fig. 3 correlates the increases in acid content with the increase in absorbance difference. These are reasonably linear correlations. The initial acid content for most films is 0.35×10^{-4} mol/g so doubling it should increase the difference in absorbance above that of the base line by 0.2 in the acid region and 0.3 in the alcohol region. There is ample sensitivity to measure that difference so the lines of Fig. 3 could be used to anticipate failure or calculate the rate constant for the increase in acid content. The acid contents with i subscripts in Table I are means of the two values calculated from the lines of Fig. 3.

Probably the interfering reflections contribute importantly to the scatter of the data about the lines in Fig. 3. Roughening the samples reduces the reflections but introduces uncertain differences in thickness. One method suggested by Addelman and Zichy[6], which we have not tried as yet, is to coat each film with a dry hydrocarbon.

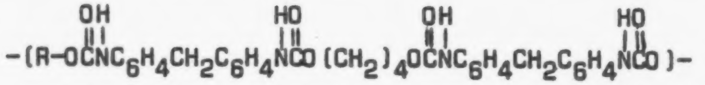
3.2 Studies with Model Binder[7]

3.2.1 Characteristics of unaged materials The binder layer of magnetic tape consists of iron oxide particles dispersed in a crosslinked polyester polyurethane. This layer is prepared by dissolving a polyester polyurethane, adding iron oxide and crosslinking agent, applying the slurry to PET film, and heating the film to evaporate solvent and cause crosslinking. The iron oxide is precoated with a wetting agent and a catalyst is used to speed the reaction. A polyisocyanate is used as the crosslinking agent. It reacts with the urethane groups to form allophanate linkages:



$$-O\overset{\overset{O}{\|}}{C}\overset{\overset{H}{|}}{N}- + -NCO \longrightarrow -O\overset{\overset{O}{\|}}{C}\overset{|}{N}\overset{\overset{O}{\|}}{C}\overset{\overset{H}{|}}{N}- \qquad (4)$$

The soluble polyester polyurethane is a block copolymer with the structure:



$$-(R{-}O\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}C_6H_4CH_2C_6H_4\overset{H}{\overset{|}{N}}\overset{O}{\overset{\|}{C}}O(CH_2)_4O\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}C_6H_4CH_2C_6H_4\overset{H}{\overset{|}{N}}\overset{O}{\overset{\|}{C}}O)- \qquad (5)$$

The group, R, is a polyester, frequently poly(butylene adipate), with a molecular weight of about 1000; it is the soft segment. The rest of structure 5 has a molecular weight of about 600; it is the hard segment and it contains the urethane groups. There are about 15 segments of each type in an average polymer molecule. Hard segments associate to some extent and make the bulk polyurethane behave as if it were crosslinked. The allophanate reaction introduces chemical bonds between hard segments, which may be on different molecules, and so generates an infinite network known as gel. Not every molecule need be part of the gel.

Our model binder lacks iron oxide, wetting agent, and catalyst and it uses a mixture of toluene diisocyanates, 20% ortho and 80% para, instead of a polyisocyanate. Nevertheless. it should respond to hydrolysis much like binder because the hydrolysis occurs in the ester linkages, which are the same in binder and model.

Polymers that have been crosslinked past the gel point are incompletely soluble. They are evaluated by measuring the fraction of material that is soluble (sol,s) and the volume fraction of gel in polymer swollen by solvent. We used these methods and also infra-red spectroscopy to measure the change in acid content. Scission of the ester linkage during degradation creates additional sol, increases the extent of swelling, and increases the acid content, which can not be measured by titration unless the polymer is nearly all sol.

One crosslinked unit per weight average molecule gives gelation[8]. Our starting polymer has number and weight average molecular weights of about 25000 and 50000 respectively, as measured by gel chromatography. Thus only 2×10^{-5} mol crosslinked units/g polymer is required for gelation. Much more crosslinking is possible because each hard segment contains four urethane groups, so there are about 60 possible crosslinking sites per molecule. A network of hard segments is expected if one urethane group in four is crosslinked. This second network should not be degraded by hydrolysis of the ester groups.

Table III lists some of the initial properties of the model binders. Quantities from left to right are: I/U, the ratio of isocyanate to urethane groups mixed together; s, the sol fraction; v, the volume fraction of polymer in a gel swollen with tetrahydrofuran; γ , the number of crosslinked units/polymer molecule; tensile strength; elongation at break; and ΔAbs/l, the difference in absorbances at 3520 and 3750 cm^{-1} divided by the thickness of the film.

The material with I/U equal to zero is starting polymer. Amounts of diisocyanate much in excess of those theoretically required for gelation were used for the models. Sol fraction decreased and the volume fraction of polymer in swollen gel increased as I/U was increased. Values of γ were calculated from s and v, by equations of Charlesby[9] and Flory[10], respectively. The Charlesby equation was used when I/U was equal to 0.14 and the Flory equation was used with the other two model binders. Sol fractions in these two polymers appeared to be zero, which prevents use of the Charlesby equation. The Flory equation will not allow for crosslinks in the sol, so it was not used when I/U was 0.14. Theoretical values of γ , assuming complete reaction of isocyanate with urethane, are 9,35, and 63 crosslinked units/polymer molecule, at I/U equal to 0.14, 0.55, and 1.10, respectively. The poor agreement with the experimental value at low I/U may be due to crosslinks within one polymer molecule and loss of isocyanate either by evaporation or reaction with inadventitious water. Agreement is better at I/U equal to 0.55 and 1.1 but our aging studies suggest the Flory equation gives too high a crosslink density in this system.

Tensile strength and elongation were measured using rectangular specimens about 2 X 0.3 X 0.01 cm. These had a tendency to tear if the crosslink density was high. The variance is about 25% at I/U equal 0.55 and 1.1 and about 10% at I/U equal 0 and 0.14.

Water contents at 35 and 85°C and 100% RH were nearly the same in the soluble polyester polyurethane and in model binders with I/U equal to 0.14 and 1.1.

Infra-red spectra of aged and unaged dry films between 3800 and 3320 cm^{-1} are in Fig. 4. Lines 1-3 are for unaged film. The large peak that is off the absorbance scale at 3350 cm^{-1} is due to NH stretching. This peak is broader in model binder than in polyester polyurethane. We did not find the acid OH stretching region at 3250 cm^{-1} useful because the NH band was so intense. A useful correlation was developed using the alcohol band at 3520 cm^{-1}. The spectra of unaged films with high crosslink density show smaller absorbance differences between 3520 and 3750 cm^{-1}. The values of ΔAbs/l in Table III quantify this result. It is reasonable because reaction between isocyanate and alcohol is more rapid than the allophanate reaction.

A small sharp peak at 2280 cm^{-1}, a region where isocyanate absorbs, was present in spectra of model binders made with I/U equal to 0.55 and

1.1. This peak disappeared during aging, presumably as a result of reaction between isocyanate and water. Spectra of the polyester polyurethane and the model binder with I/U equal to 0.14 lacked this peak.

A question of importance because of the autocatalytic effect of acid, is whether the isocyanate reacts with carboxylic acid? This is present in the starting polyurethane at a concentration of about 10^{-5} mol/g. Schollenberger and Stewart[11] found no reaction between acid and isocyanate during urethane preparation. Here reaction would compete with the allophanate reaction, which is slow. We aged the polyurethane until it had an acid content of 6 X 10^{-4} mol/g and then treated it with enough monoisocyanate (used so the product would be soluble) to react with all the urethane, alcohol, and acid present. After reaction for one week at 100°C the acid content was only 0.25 X 10^{-4} mol/g. Apparently acid can be destroyed by isocyanate.

3.2.2 Aging effects at 85°C in model binders Pieces of the film made with I/U equal to 1.1 were aged in sealed glass tubes above well dried Molecular Sieves in vacuum, dry nitrogen, and dry air. Samples were also aged in wet air at 100% RH and above water vapor in the absence of air. Three exposure times were used: 18.7, 38.7, and 56.7 days. None of the samples that were aged dry swelled less in solvent than it did before aging. Pieces of film made with I/U equal to 0.14 were aged for 10.4 days in dry air and in wet air at 100% RH. The sol fraction of the film aged dry was the same as before aging. Thus our conclusion is that model binder does not crosslink when aged dry. This is a distinctly different result than obtained with magnetic tapes.

The samples aged wet became quite highly colored during aging whereas those aged dry changed very slightly. Fig. 5 illustrates this effect in the films made with I/U equal to 1.1. The unaged specimens and those aged dry barely show in Fig. 5 because they are nearly colorless. Samples aged in vacuum are like those aged in dry N_2. Samples aged wet were at 100% RH except as noted. Discoloration is worse in wet air than in air-free water vapor. There have been studies of the discoloration of polyurethanes during aging[12,13] but the authors did not investigate the effect of moisture.

Samples aged for long periods at high humidity became hard and brittle. Their acid contents actually were less then those of samples aged for shorter times. Our speculation was that the molecules had degraded so much that polyester evaporated and dissolved in the aqueous phase, thereby raising the glass temperature of the remaining polymer and decreasing its acid content. Samples were submitted for nitrogen analysis; results are in Table IV. The increases in nitrogen content support the hypothesis. Crosslinking and lower RH appear to reduce the effect.

Fig. 6 shows how tensile strength and elongation change with time in samples aged at 100% RH. The lines connect sequential points for each value of I/U. Values for the crosslinked samples usually increase initially. It seems reasonable that scissions in a tightly crosslinked polymer initially increase extensibility. The effect on tensile strength probably is due to decreased sensitivity to edge imperfections in a more extensible polymer. Additional aging causes a rapid decrease in both T and E at times that increase with I/U.

Fig. 7 shows values of T and E after aging at 25% RH. Longer times were required to give the same effects than at 100% RH. The elongations of the two more densely crosslinked samples remain large. Less extensive degradation at 25% than at 100% RH probably gave products that remained in the polymers and softened them. Polymers aged for the longest times are probably too soft to be satisfactory binder even at high I/U.

Agings were also done at 50% RH with results intermediate between those at 25 and 100% RH. All samples eventually broke at low elongation.

Fig. 8 shows the sol fraction of the two more densely crosslinked samples after aging at 25, 50, and 100% RH. The material with I/U equal to 0.55 eventually becomes completely soluble at all RH whereas the other material appears to reach a final sol fraction equal to 0.6. The weight fraction of hard segment plus added toluene diisocyanate is 0.42 when I/U is 1.1. Accordingly, we feel that the material that does not dissolve is primarily crosslinked hard segment, although some hard segment and some ester are in sol and gel respectively. The fact that the polymer with I/U equal to 0.55 did not form permanent gel, even though it had twice the isocyanate sufficient to do so, suggests that at least half the isocyanate was wasted. Crosslinks between urethane groups within the same hard segment or molecule could account for this. An additional implication is that the values of γ in Table III for materials with I/U equal to 0.55 and 1.1 are much too high. The reasons for the failure of the Flory equation may be connected with the preferred association of hard segments in polyester polyurethanes. We suspect that chains coming from hard segment blocks interfere with one another and so do not swell to normal equilibrium.

Values of the sol fraction can be used to calculate the number of scissions. We did this using the γ of Table III [7] but now think the results were wrong because the initial crosslink densities were too high. Mol scissions/g reached values as high as 4 X 10^{-3} even at 25% RH. This is much higher than found in polyester polyurethanes at the same RH[4]. More reasonable values are obtained if γ is about 10 for unaged model binder with I/U equal to 0.55. To get this would require that the sol fraction be 0.01, which is too small to be significant. The corresponding density of crosslinked units, γ/M_0, is 4 X 10^{-4} mol/g if M_0 is 25000 g/mol. The polymer should become completely soluble during hydrolysis when γ is 0.5, since it has a most probable distribution. The concentration of crosslinked units will be unchanged if only the ester groups hydrolyze. Therefore the molecular weight will be 0.5/(4 X 10^{-4}) or 1250 when complete solubilization occurs. There should be one acid group per molecule in the degraded material, making [A] equal to 8 X 10^{-4} mol/g.

Acid content can be measured by titration of soluble polymers. Values obtained by titration of crosslinked, partly soluble polymers are not expected to be valid because the base will not get into the polymer. Infrared spectroscopy appears to be useful in measuring the increase in acid content of such materials.

Lines 4-6 in Fig 4 are infra-red spectra of aged polymers. Comparisons with the spectra of the corresponding unaged polymers indicate the aged samples have a larger absorbance at 3520 cm^{-1}, in the alcohol OH stretching region, and at 3717 cm^{-1}. The absorbance of each sample between 3700 and 6500 cm^{-1} is substantially constant but is higher for the aged films. The cause of this raised absorbance plateau is uncertain but we have treated the flat region as the baseline and measured ΔAbs/l as for the unaged polymers. Titrations for acid were performed on soluble polymers. Acid contents were obtained with unaged starting polymer, I/U=0, and aged polymers with I/U=0, 0.14, and 0.55. As many alcohol groups should form as acid groups, according to reaction 1. Thus one should expect the increase in acid content will be proportional to the increase in the absorbance difference,i.e., $\Delta\Delta$Abs/l. Furthermore, if the original acid content is much less than the acid content after aging, as seems reasonable, then the acid contents should be proportional to the increase in absorbance difference. This is shown to be approximately true in Fig. 9. The line in this figure was used to calculate acid contents of polymers that were not completely soluble.

Fig. 10 is a plot of acid content vs. time at 85°C and 100% RH. Acid contents were determined by titration or by use of Fig. 9. Lines are calculated by Eq. 2, using values of $[A_0]$ and k listed on the plots. The intent is to fit only the early points. Figures 11 and 12 contain similar results from samples aged at 85°C and 50 and 25% RH, respectively. Note that at 25% RH the last [A] determined for the polymer with I/U equal to 0.55 is about 7×10^{-4} mol/g. The conclusions drawn from these plots are that $[A_0]$ and k are less for the densely crosslinked films.

Presumably reaction between acid and isocyanate reduces $[A_0]$. Reasons for the reduction in k are speculative, but it is suggested that the rate constant for esterification, i.e. the reverse of reaction 1, is effectively greater in a densely crosslinked gel than in an uncrosslinked polymer because the acid and alcohol can not separate normally because of physical constraints. The apparent result would be to decrease k, the rate constant for hydrolysis.

Preliminary tests of this hypothesis have been made by pre-aging model binder and re-aging it at 0% RH. Under this condition the acid content should decrease and hydrolysis should be absent. Reaction is just the reverse of reaction 1. The differential equation connecting [A] and time is[4]:

$$-(d[A]/dt) = k'[A]^2([H_0] + [A]) \quad (6)$$

Here $[H_0]$ is the alcohol content before the initial aging and k' is the rate constant for the back reaction. Acid concentration is squared because acid catalyzes hydrolysis and so must catalyze esterification.

Results in Table V were obtained by integrating Eq 6 and solving the resulting equation for k', using $[A_0]$ as the acid content at the start of the re-aging period and [A] and t as acid content and time after re-aging[4]. Thus each k' is calculated from two points, $[A_0]$,0 and [A],t. The $[H_0]$, which are required, were calculated as follows. The acid content for uncrosslinked polymer was determined by titration and found to be 10^{-5} eq./g. The molecular weight is 20,000-25,000, so there are about 10^{-4} mol of end groups/g polymer. Only 10% of these are acid groups so the concentration of alcohol groups was taken as 10^{-4} mol/g. It was then assumed that ΔAbs/l, in Table III, was proportional to the alcohol content so $[H_0]$ for unaged crosslinked film is 10^{-4} times the ratio of the (Abs/l)'s.

The final column lists the k'. Results probably are not very accurate so the first five listings are regarded as not differing significantly. The last three listings indicate that k' is larger for the most densely crosslinked material. However, the effect seems to be less the greater the initial $[A_0]$, i.e. the greater the extent of pre-aging. The implication is that hydrolysis will eventually reduce k' to its value for uncrosslinked polymer. The second listing for k' uses 10^{-4} mol/g for $[H_0]$, which we regard as known only approximately. Larger $[H_0]$ does not eliminate the larger k' of polymer with I/U equal to 1.1.

Previously it was found that k' in uncrosslinked polyester diols and polyurethanes depended on RH[4]. Consequently, the values of k' in Table V probably should not be used at any other RH than zero.

Model binders are being aged at 60 and 35 °C. Preliminary results at 60 °C are like those at 85 °C but a five fold greater time is required to accomplish the same result. No significant degradation had occurred at 35 °C.

3.3 Magnetic tapes

3.3.1 Unaged tapes Characteristics of unaged tapes are listed in Table VI. The values are nearly the same as those in the last report. Changes were made as additional measurements affected the average results. Tape 1 has binder with carbon on the surface opposite the one with magnetic oxide. The other tapes do not have this coating. Several rolls of Tape 5 had very low adhesive force between binder and PET base so the group has been divided into 5A and 5B.

The weight of the binder layer was determined by immersing tape in acetone, scraping off the swollen layer, and weighing the PET base. The organic content of the binder layer was determined by burning off the binder in air. It is possible that some reduction of the iron oxide may have occurred during this operation, which would result in an unknown error. The quantities in the column headed "Sol in Org BL" are probably somewhat more than the sol content of the polymer that makes up the binder layer because of the extraction of additives, such as lubricant, catalyst fragments, and oxide wetting agent.

The acid content of the sol from Tape 4 was measured by titration and found to be 8 X 10^{-5} mol/g. A lower value was expected because polyester polyurethanes generally are made with acid contents approximately equal to 10^{-5} mol/g. Lower molecular weight components, which have more chain ends and so more acid, tend to remain as sol during crosslinking. This makes the acid content of the sol different from that of the whole polymer but even if there is no acid in the gel the overall value is about 5 X 10^{-5}. Acid contents of sol from other tapes were not measured because they are smaller fractions of the organic component of the binder layer.

The binder layer can be removed from the PET base by immersing tape in the proper solvent mixture for about 60 seconds. A mixture containing three volume percent water in hexafluoroisopropanol works for all except Tape 4. The binder floats off and curls up but has enough strength so it can be drawn flat onto a 10 mil-thick Teflon sheet, that is also immersed. Hexafluoroisopropanol is sorbed by the skin and is a poisonous vapor, so care must be exercised during these operations. Binder on Tape 4 is very fragile when highly swollen, because of its low crosslink density. A mixture of 10 volume percent water in acetone swells the binder layer of Tape 4 adequately. A small amount of material is actually dissolved during the removal operations. The use of mixed solvent and non solvent reduces this to a relatively small fraction of the total sol.

Fig. 13 compares the infra-red spectra of binder layer from Tape 1 and the soluble polyester polyurethane used to make our model binder. The spectra are very similar, except for the scattering due to the oxide particles, which results in a decreasing baseline, and absorption due to the magnetic oxide at about 600 cm^{-1}. There is also a broad, weak peak at 2200 cm^{-1} in the spectrum of the binder layer that is not in that of the polyurethane.

Fig. 14 compares spectra of binder layers from six kinds of tape. All spectra are very similar but there are differences in the weak absorptions between 2600 and 1800 cm^{-1}. The source of these absorptions is unknown. Isocyanates and carbodiimides have relatively sharp absorptions at 2270 and 2170 cm^{-1}, respectively. Isocyanate hydrolyzes to amine at room temperature, so it is unlikely to be present even in unaged tapes. Carbodiimide is used to stabilize polyester polyurethanes and might be an additive, but a narrower peak should result. We had hoped to study the degradation of the binder layer by using the absorption due to alcohol groups, as in model binder, but these absorptions are so weak compared with the scattering that the approach does not appear promising. Signal to noise was much improved by making 10,000 scans, which requires about two hours for each spectrum but even then the desired absorbance difference was not known precisely. Additionally, our aging data suggest that adhesion of binder layer to PET base may be the limiting factor in tape life.

3.3.2 Aged magnetic tapes Tapes 1-5A were aged in vacuum, dry nitrogen, dry air, wet air (100% RH), and air-free water vapor at 85° C. Aging under dry conditions caused a reduction in the sol content, presumably due to crosslinking. Wet air and water vapor caused approximately equal increases in sol content.

An aging temperature of 85° C appeared more severe than necessary or desirable, since our interest was in changes at ambient temperature. Most of our results now involve agings at 60 and 35° C.

Fig. 15 shows sol contents after aging at 60° C and 100% RH. Most of the tapes reach 5% sol in about 100 days and then give slightly less sol on additional aging. A sol content of 5% corresponds to about 60-70% of the organic component of the binder layer being soluble. Tape 2 reaches only 3% sol, which corresponds to about 55% soluble binder. Even Tape 4 binder, which is 66% soluble to start with, never becomes more than 70% soluble. These results resemble behavior of the most highly crosslinked model binder.

Sol fractions of tapes aged at 60°C and 30, 15, and 0% RH decreased with time, implying that the binder crosslinked. Sol extracted from unaged Tape 4 gelled when aged at 85°C and 0% RH, confirming that crosslinking occurred.

Sol contents of Tapes 1,2,3,4, and 5A are 1.8, 2.4, 4.0, 5.4, and 2.3%, respectively, after about 250 days aging at 35°C and 100% RH. The infra-red spectra of the extracted sol are like the spectrum of the polyester polyurethane in Fig. 13 except for a small sharp peak at 2250 cm^{-1} in the former spectra. Attempts to determine the acid contents of sol extracted from aged tapes by titration have not been successful because color changes during titration preclude use of indicators and no sudden change occurs in electrode potential during potentiometric titration.

Deteriorating adhesive force between binder and PET base could cause failure of the tape. Our method of measuring this force is to apply a 20-30 cm length of 3/8-in wide embossing tape to the center of the oxide layer of the 1/2 in-wide magnetic tape and then separate the two tapes in a tensile testing machine. A high crosshead speed helps start the separation of binder layer and PET; 20 and 40 in/min were used. The force is initially high but decreases quickly and is within about 25% of some average value during most of the pull. There is considerable oscillation of the pen during the pull because the separation occurs as a series of stops and starts. Fig. 16 shows the recorder trace from three such measurements.

Unaged Tapes 2, 4, and 5A do not lose binder layer during these experiments. The other unaged tapes lose binder, sometimes by failure between binder layer and PET (adhesive) and sometimes by failure within the binder layer (cohesive). Fig. 17 shows the behavior patterns in unaged tapes that do lose binder during the measurement. Most failures are mainly adhesive or mainly cohesive but not exclusively either. Sometimes horizontal or vertical strips of binder layer are left on the PET. There have been cases in which the type of residue has changed within one pull. Fig. 17 contains an example of this. No convincing rationalization of these phenomena has occurred to us.

The measured adhesive or cohesive force decreases during aging in a way that depends on temperature and RH. Binder layer fell off all tapes aged at 60 °C and 100% RH for one year. These tapes were obviously not useful. Fig. 18 and 19 show the time dependence of binder adhesion (or cohesion) after aging at 60 °C and 30 and 15% RH, respectively. Great decreases from the initial values occur. Very low values, about 10 N/m, are reached for Tapes 3 and 6. Aging at 15% RH makes the sol content decrease, so changes in sol content probably will not be reliable indicators of tape reliability.

Values of binder adhesion exceed 80 N/m for all tapes after nearly 500 days at 35 °C and 100% RH. Aging at lower RH for about one year leaves still higher values.

Experiments with aged tapes indicate that write and read problems occur when the binder adhesion value has decreased to about 10 N/m. The programmed write-read sequence, described in the Experimental section, failed after 14 passes of Tape 3, aged until the binder layer adhesive force was 10 N/m. There was binder layer on the heads and when it was removed additional write-read passes were made. Failure again occurred before 25 passes of each type were made. Other aged tapes would run through 25 passes. These results imply that large decreases in binder adhesion can occur before tapes become useless. Consequently, binder adhesion can be used to monitor tape condition.

4.0 Discussion

4.1 PET All results to date indicate that the type of PET now being made will last several centuries under the mild conditions anticipated for storage of archival materials. The extrapolation through the glass temperature is still a source of uncertainty and will remain so until some determination, probably of the acid content, gives the rate constant at a lower temperature than 55 °C.

It is emphasized that the excellent physical properties of PET may depend on a rather specific combination of orientation and crystallinity. Any changes might result in a material that has different sensitivity to hydrolysis. Results obtained with the electrographic films C may illustrate this. These films fail physically before the other films and have significantly different crystallinity than the other films, as described in the first report.

The infra-red technique described above can be used to monitor degradation, if that becomes desirable. It is necessary to remove any film coating from an area sufficiently large to transmit the beam. The two-fold increase in acid content is a reasonable failure criterion, excepting films C, so long as films of the present type are in use. Changes in film characteristics would require that the failure criterion be reestablished.

4.2 Model Binder The model binders behaved in a manner qualitatively anticipated from results obtained earlier with soluble polyester polyurethanes. There is autocatalysis due to the acid catalyzed hydrolysis. However, times to reach specific acid contents are longer because of the lower initial acid content and, less conclusively, also because of the lower effective rate constants for hydrolysis, Fig. 10 - 12 and Table V. An acid content of 8×10^{-4} mol/g was obtained after long aging of the film with I/U equal to 0.55 at 85 °C and 25% RH. This is about the same as obtained at equilibrium with the soluble polyester polyurethane used to make the model binder[4]. Highly crosslinked model binders became soft and weak at 85 °C even at 25% RH but did not appear to crystallize when cooled to room temperature as did the soluble polyester polyurethanes. Degraded model binder contains allophanate branches which may prevent crystallization. The presence of a network that does not hydrolyze in the most highly crosslinked model did not prevent severe deterioration of the physical properties. Thus the aging results to date indicate that crosslinked polyester polyurethanes do not have sufficiently good physical properties at equilibrium to remain permanently acceptable as binder layer for tape. The main uncertainty in this conclusion is due to the lack of a complete set of data at other temperatures. Such data are being obtained.

4.3 Magnetic tapes Tape binder appears to crosslink at humidities at which crosslinked polyester polyurethanes degrade. One explanation might be that initial acid and alcohol concentrations in the binder are sufficiently high to drive the reaction toward crosslinking. We can make an estimate of what is required to do this. The relation governing equilibrium is[4]:

$$k[E][W] = k'[A][H] \qquad [7]$$

Here [E] and [W] are ester and water concentrations and the other quantities are as defined above. Therefore, [A][H] at equilibrium is k[E][W]/k'. Values of [E], k[W], and k' are in Tables I and IV of reference[4]. From them the product [A][H] is calculated to be 8.2×10^{-7} mol^2/g^2 at equilibrium at $85^{o}C$ and 25% RH. Consequently, [H] equals 8.2×10^{-2} if [A] equals 10^{-5} mol/g. A ten-fold greater acid concentration, which is twice the value found for the binder of Tape 4, would require proportionately fewer alcohol groups. Such concentrations seem impossibly large; pure butane diol, for example, has a concentration of alcohol groups equal to about 2×10^{-2} mol/g. Therefore, we think some process other than acid and alcohol reacting to give ester is required to explain the crosslinking observed by Cuddihy at 0 and 15% RH[2] and by us at 0, 15, and 30% RH.

Our original speculation was that the iron oxide accounted for crosslinking. However, data in the previous report showed that a sample of the kind of iron oxide used in tape manufacture actually increased the hydrolysis rate of the polyester polyurethane.

Finding that extracted sol absorbs at 2250 cm^{-1} but that polyester polyurethane does not, suggests that an additive which might cause the crosslinking is present in the extract. Absorption between 2200 and 2300 cm^{-1} is not very common. Isocyanate and carbodiimide are two possibilities and either could cause crosslinking if multifunctional. However, isocyanates react with atmospheric moisture and the only polycarbodiimide we have experience with absorbs at 2170 cm^{-1}. Therefore, such compounds seem to be ruled out.

The cause of the crosslinking is still not known.

Apparently tape lifetime is limited more by binder adhesion than by the sol content of the binder. Bertram and Cuddihy reported that tapes with more than 1.5% sol, based on the total tape weight, became difficult to use[3]. Tapes 3, 4, and 6 have more sol than that before aging and they perform well. Furthermore, the sol content of Tape 4 does not change much on hydrolysis. Thus sol content does not appear to be a useful quantity for lifetime prediction. Binder adhesion has a large range, from more than 800 to about 2 N/m, with failure occurring somewhere between 10 and 50 N/m. The measured values are not very precise but the method probably can be improved. Some error in the prediction is tolerable because tape is marginally useful even after considerable loss of adhesion has occurred.

Our method of estimating tape lifetime will involve measuring binder adhesion after aging at different temperatures and humidities and correlating the measurements with the ability of the tape transport to process the tape. A decrease to some level of binder adhesion will be defined as ending tape life. Rates of decrease and tape lifetimes will be known as functions of temperature and humidity. Extrapolation by means of the Arrhenius relation will give values under the desired conditions. This approach is empirical but it is probably the best that can be done, given the variation in tape characteristics.

5.0 Future work

Aging of PET at 55 and 35°C will continue. The main effort will be to improve the infra-red method. Some work will be started to better understand the deterioration of the coatings.

Aging of model binder will continue at 60 and 35°C. The main concern will be whether variations with temperature and humidity extrapolate so as to change our conclusion that crosslinked polyester polyurethanes will eventually hydrolyze to useless materials at ambient conditions.

An attempt will be made to estimate the lifetime of magnetic tapes as outlined above. Experiments will be performed with extracts from tapes to try to understand the crosslinking mechanism.

6.0 Conclusions

PET films as currently made for photographic and electrographic use should last more than 1000 years if stored at 20-25°C and 50% RH. The lifetimes of the coatings, which bear the information, do not appear to be that long and are unknown.

Magnetic tape lifetime appears to be a function of binder adhesion. A program has been suggested to base lifetime prediction of magnetic tapes on variations of binder adhesion with temperature and humidity.

Experiments with crosslinked polyester polyurethanes indicates that these materials will not stabilize at a tolerable extent of hydrolysis even at low humidity. This conclusion is based on results at only one temperature, 85°C. Experiments are continuing at other temperatures with these materials.

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Table I

PET Films at 55 °C and 100% RH

Material	Time Days	T MPa	E %	10^4[A] eq/g	k %/day
Film base	0	204	144	0.35	--
	586	190	128	0.44	0.037
	1105	165	106	0.54_i	0.039_i
Microfilm A	0	200	126	0.31	
	660_s	163	100		
	660	167	96		
	1105_s	166	90		
	1105	165	85		
Microfilm B	0	193	122	0.32	
	660_s	175	116		
	660	172	102		
	1105_s	171	88		
	1105	187	99		
Encapsulating Film	0	177	80	0.37	
	660	145	83		
	1105	151	73	0.57_i	0.039_i
Uncoated Electrographic C	0	116	185	0.41	
	660	110	142		
	1105	110	5	0.68_i	0.046_i
Coated Electrographic C	0	167	105	0.48	
	660	150	78		
	1105	140	68		
Coated Electrographic D	0	201	99	0.34	
	1040	177	70		

Subscripts:
i, From FTIR measurements; s, stripped of emulsion layer before aging.

Table II

Acid Content, Elongation at Break and Absorbance Difference[1] in PET Aged in Boiling Water

Time Days	Elongation %	[A] 10^4 eq/g	ΔAbs_1[2]	ΔAbs_2[3]
0	142	0.36	0.33	0.27
3	130	0.45	0.45	0.31
5.9	135	0.55	0.54	0.36
9.7	103	0.73	0.62	0.49
14.0	40	1.05	0.79	0.60
17.0	Brittle	1.41	0.98	0.76

Superscripts:

(1) From spectra of three stacked films, each 0.004 inch thick.

(2) ΔAbs_1 - Absorbance at 3542 cm^{-1} minus that at 3717 cm^{-1}.

(3) ΔAbs_2 - Absorbance at 3256 cm^{-1} minus that at 3717 cm^{-1}.

Table III

Initial Properties of Polyurethane Films

I/U mol/ratio	s fr	v fr	Y X ℓ/pol	T M Pa	E %	ΔAbs/ℓ cm^{-1}
0	1	-	0	63	1200	6.8
0.14	0.79	0.054	0.6	73	900	5.8
.55	-0	0.38	42	45	370	0.045
1.1	-0	0.47	71	40	130	0.15

Table IV

Elemental Composition Change at 85 °C

I/V mol/ratio	Time Days	RH %	10^5[A] mol/g	N %
0	0	-	1	3.6
0	48	100	80	5.6
1.1	0	-	<1	6.1
1.1	57	100	53	7.1
1.1	113	50	52	6.0

Table V

Recombination of Acid and Alcohol at 85 °C in Dry Polyurethane

(60 days except as indicated)

$$-(d[A]/dt) = k'[A]^2([H_o]+[A])$$

I/U	10^6 H_o	10^4 A_o	10^4 A	10^{-5} k'
mol ratio	mol/g			$g^2/mol,^2d$ *
0	100	5.1	1.9†	1.3
0	100	5.1	1.1‡	1.1
0	100	2.3	1.1	3.1
0.14	86	1.9	1.2	2.2, 2.1
0.55	0.67	2.5	1.75	1.4, 0.9
1.1	2.2	6.6	1.1	6.6, 4.2
1.1	2.2	1.25	0.59	18, 8.2
1.1	2.2	0.62	0.29	73, 22^3

†) 68 d, ‡) 219 d, *) 2nd value uses $H_o = 10^{-4}$ mol/g

Table VI

Characteristics of Unaged Magnetic Tape

Tape	Binder Layer (BL) wt%	Sol Contact wt%	Binder Adhesion N/m[1]	Organic in BL wt%	Sol in Org BL wt%
1	20[2]	0.7	325	30[3]	8[4]
2	23	1.3	>800	24	24
3	32	2.4	150	25	30
4	24	4.6	>800	29	66
5A	28	0.7	>450	26	9.6
5B		1.0	35		
6		2.6	160		

[1] 1 N/m = 1.02 g/cm

[2] Not including the back coat that is 6% of the tape weight.

[3] Oxide binder only

[4] Assuming half the back coat is carbon.

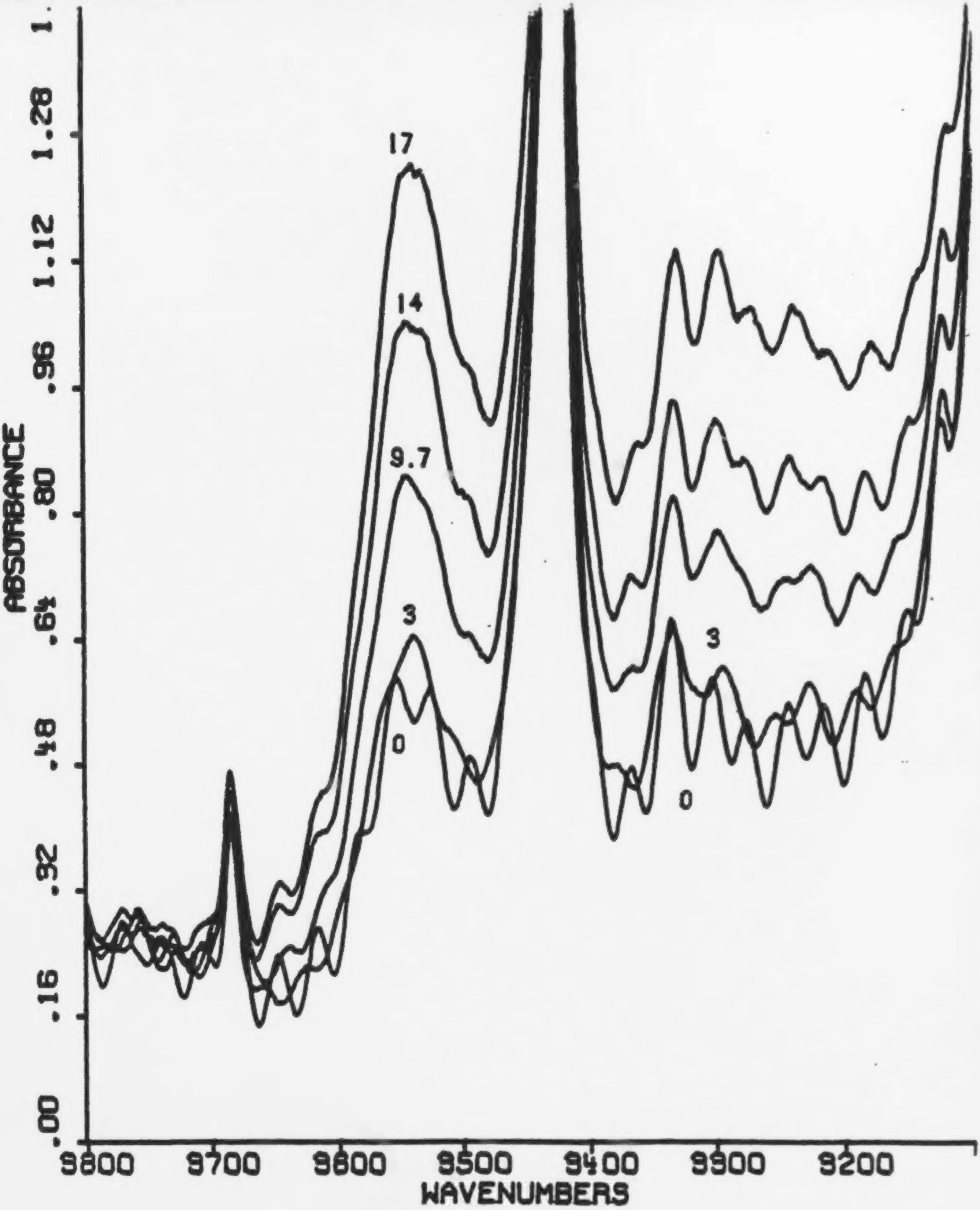


FIG. 1 INFRA-RED SPECTRA OF PET AFTER AGING IN BOILING WATER. 2-CM^{-1} RESOLUTION. CURVES LABELED WITH AGING TIME IN DAYS.

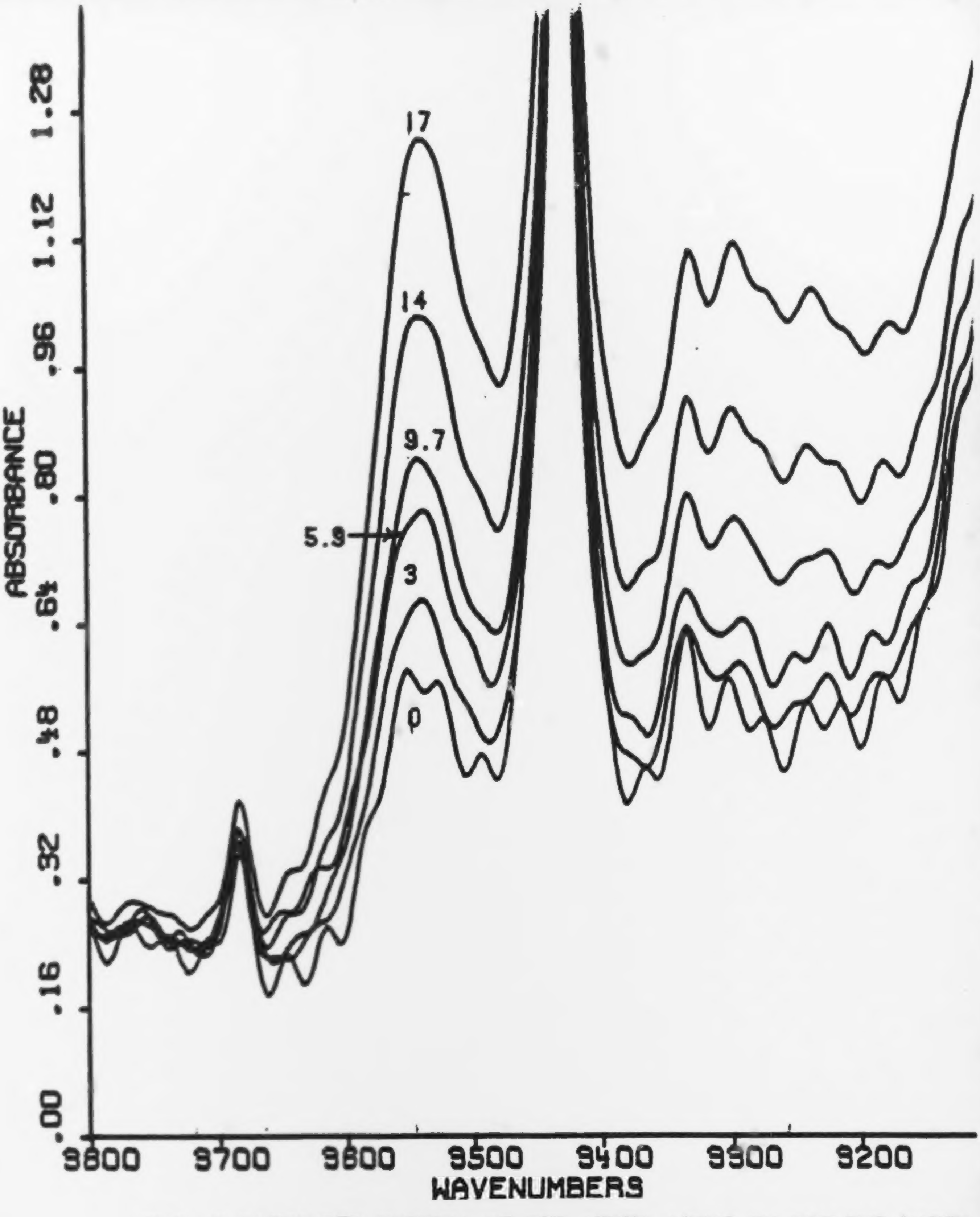
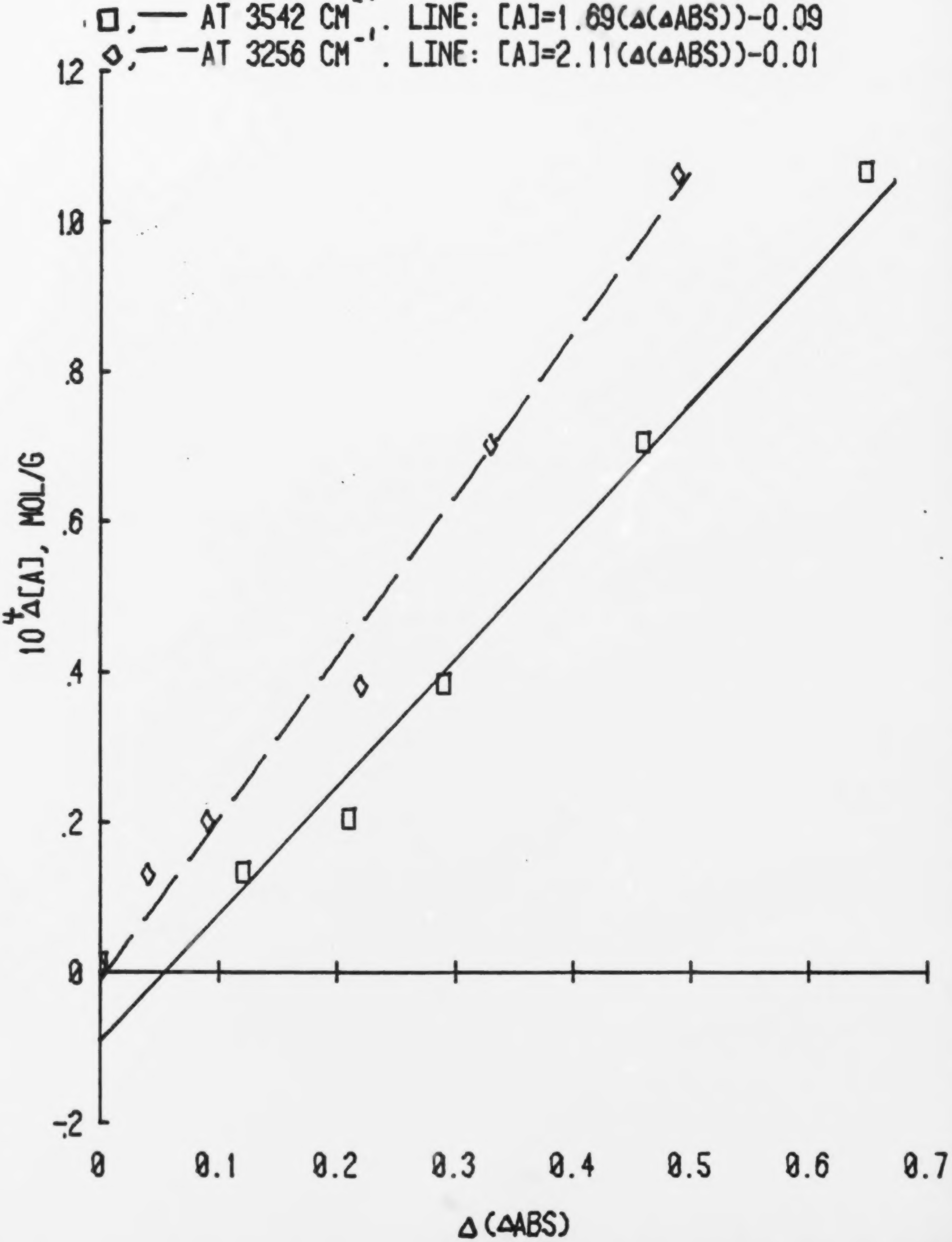


FIG. 2 INFRA-RED SPECTRA OF PET AFTER AGING IN BOILING WATER 8-CM^{-1} RESOLUTION. CURVES LABELED WITH AGING TIME IN DAYS,

FIG. 3 CHANGE IN [A] VS CHANGE IN ΔABS



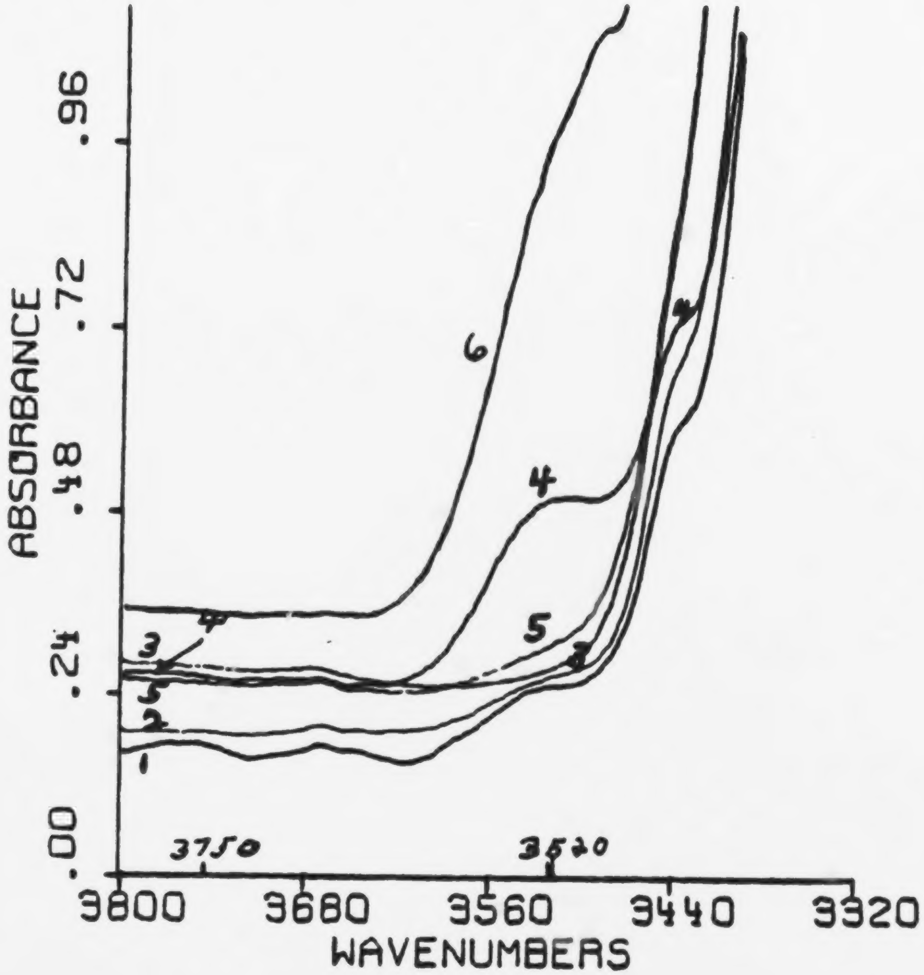
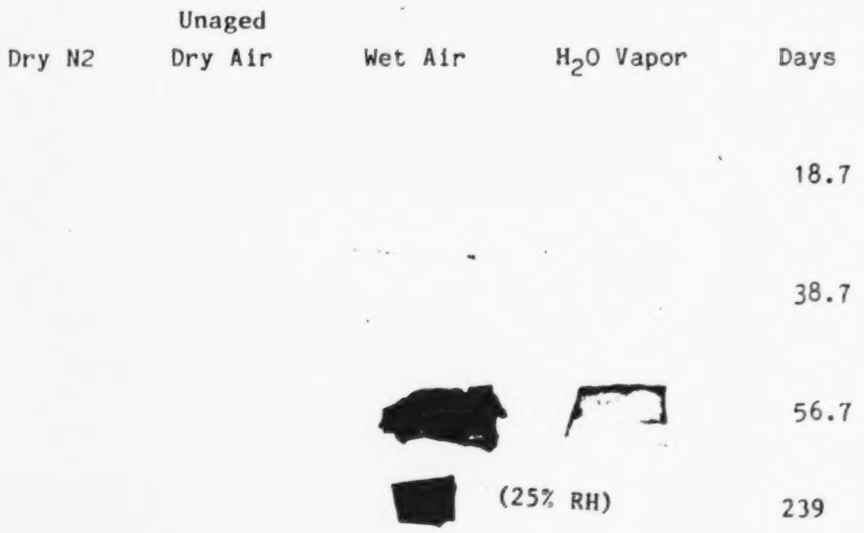


FIG. 4 FTIR SPECTRA OF URETHANE FILMS. UNAGED: 1. I/U=0, l=0.012 CM; 2. I/U=0.14, l=0.013 CM; 3. I/U=0.55, l=0.015 CM. AGED AT 85°C: 4. I/U=0.14, l=0.010 CM, 25% RH, 50 DAYS; 5. I/U=0.55, l=0.015 CM, 25% RH, 59 DAYS; 6. MULTIPLY ABSORBANCE BY 2, I/U=0.55, l=0.015 CM, 50% RH, 87 DAYS.

FIG. 5

Color Development in Crosslinked Polyurethane,
(I/U) = 1.1, at 85 °C



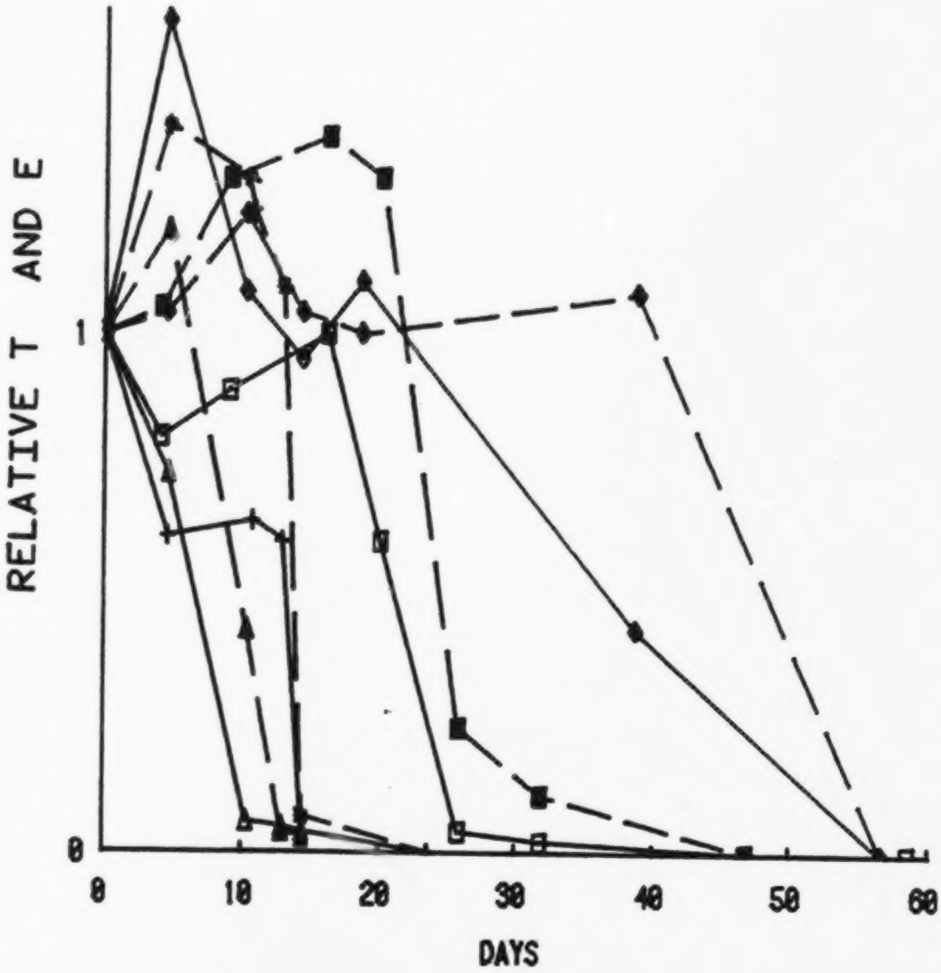


FIG. 6 T AND E RELATIVE TO INITIAL VALUES
VS. DAYS AT 85 C AND 100% RH
T, UNSHADED SYMBOLS AND ———— ;
E, SHADED SYMBOLS AND —— —— ——;
△ , ▲ I/U=0; + , ✱ I/U=0.14; □ , ■ I/U=
0.55; ◇ , ◆ I/U=1.1.

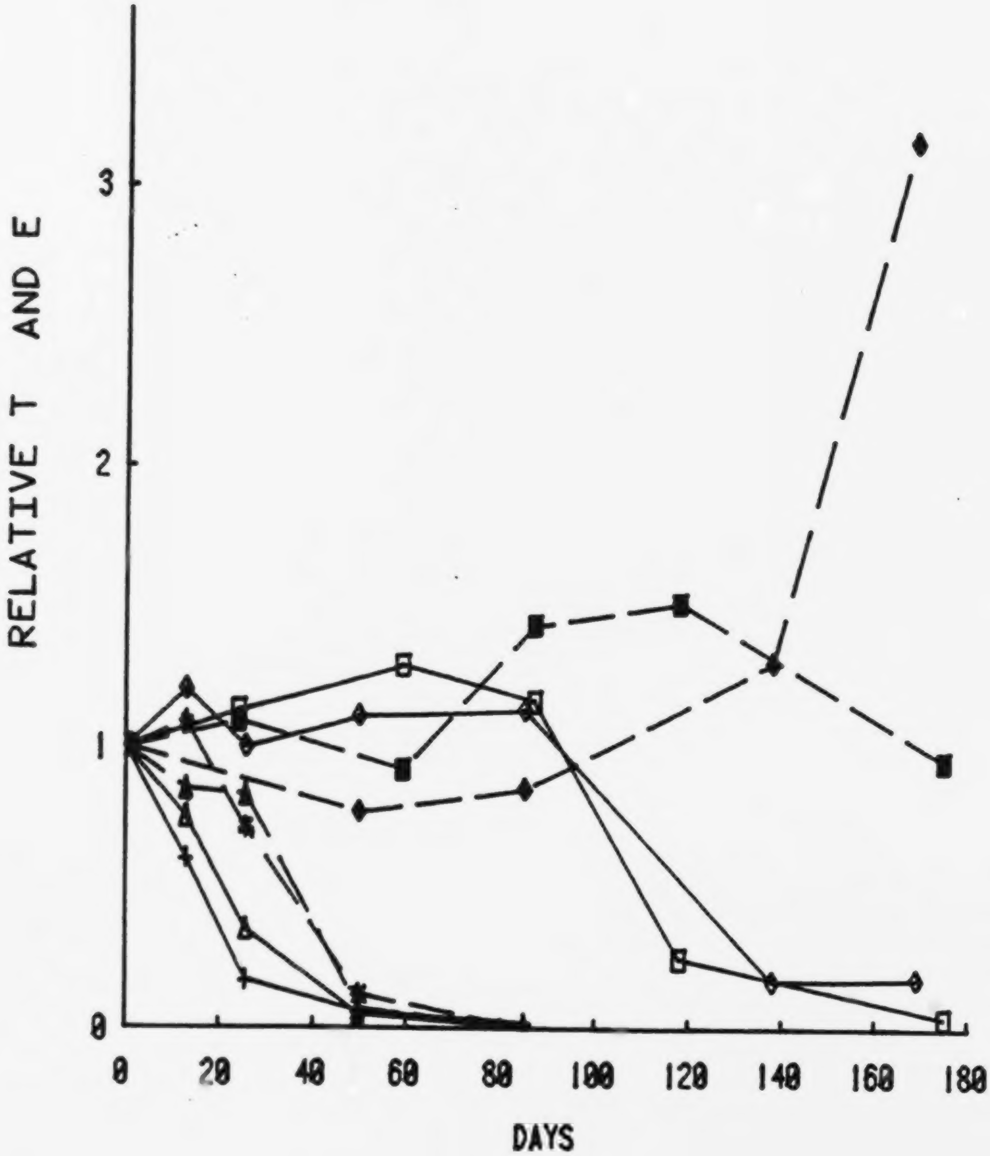


FIG. 7

T AND E RELATIVE TO INITIAL VALUES
VS. DAYS AT 85 C AND 25% RH
T , UNSHADED,——; E, SHADED,— —;
△ , ▲, I/U=0; + , ✱, I/U=0.14;
□, ■, I/U=0.55; ◇ , ◆, I/U=1.1

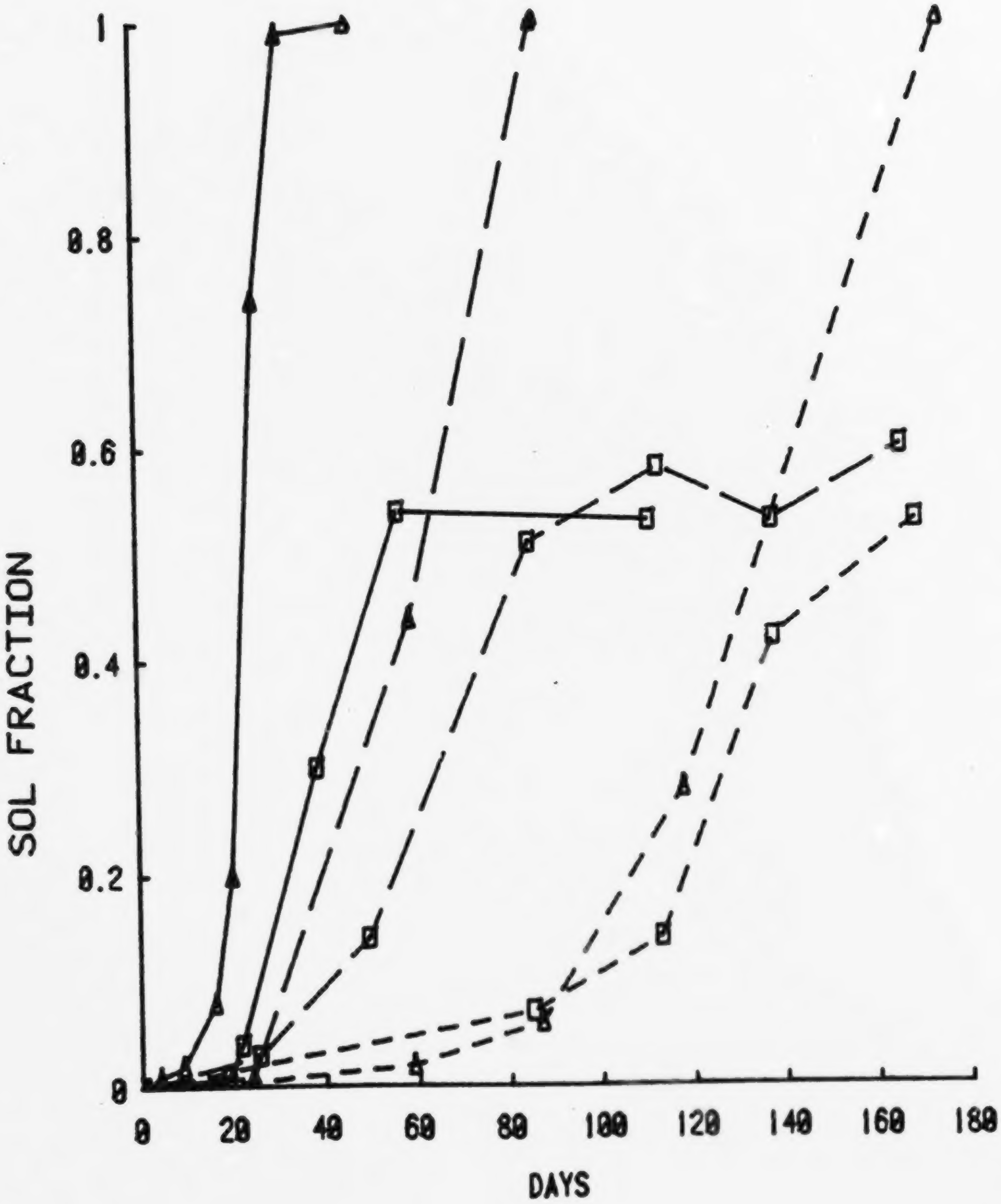


FIG. 8 SOL FRACTION VS TIME AT 85 C
Δ, I/U=0.55; □, I/U=1.1
100% RH ———, 50% RH — —, 25% RH - - - -.

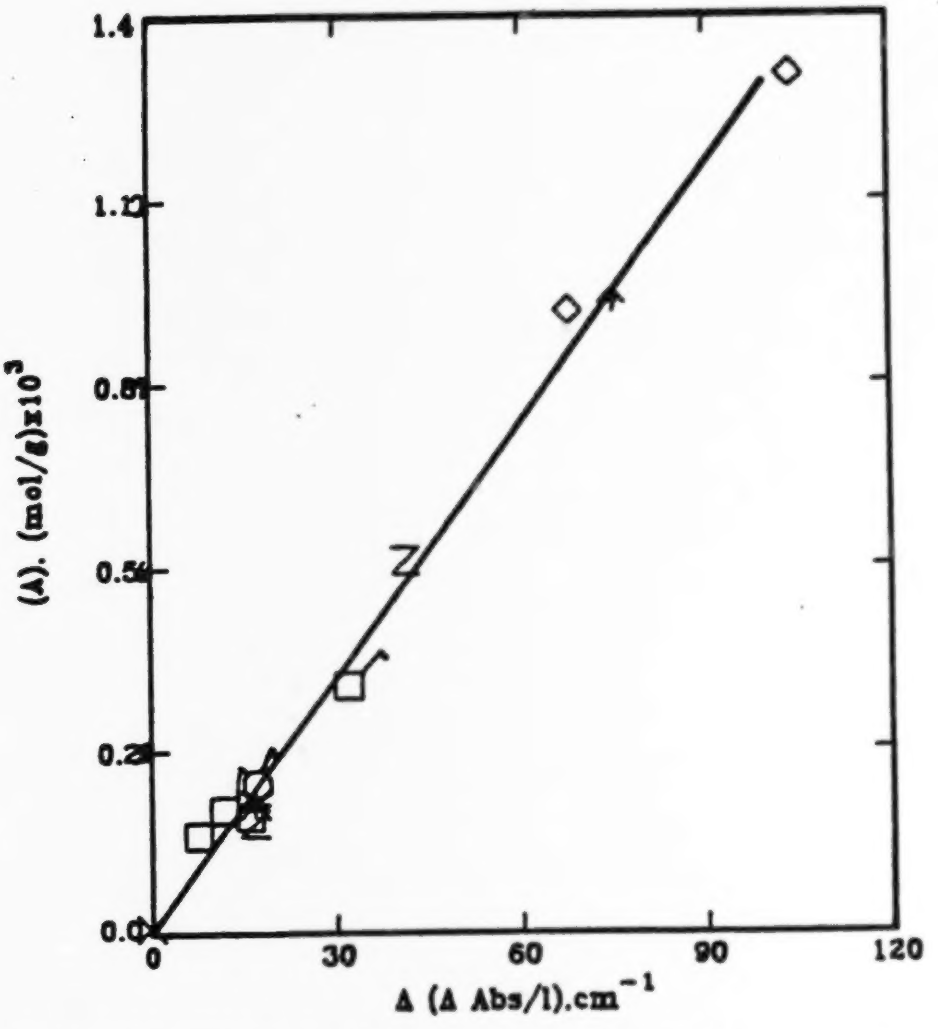


Fig. 9 Acid content vs. increase in Δ(absorbance/film thickness) during aging.
I/U=0:X,unaged; ✱,85C, 25% RH; ♂, 60C, 100%RH. I/U=0.14:
⊐,■,Z; 85C, 100, 50, 25% RH; ⊏, 60C, 100%RH. I/U=0.55:
◇,⚲; 85C, 100, 50% RH. Line: [A]=0.013XΔ(ΔAbs/l).

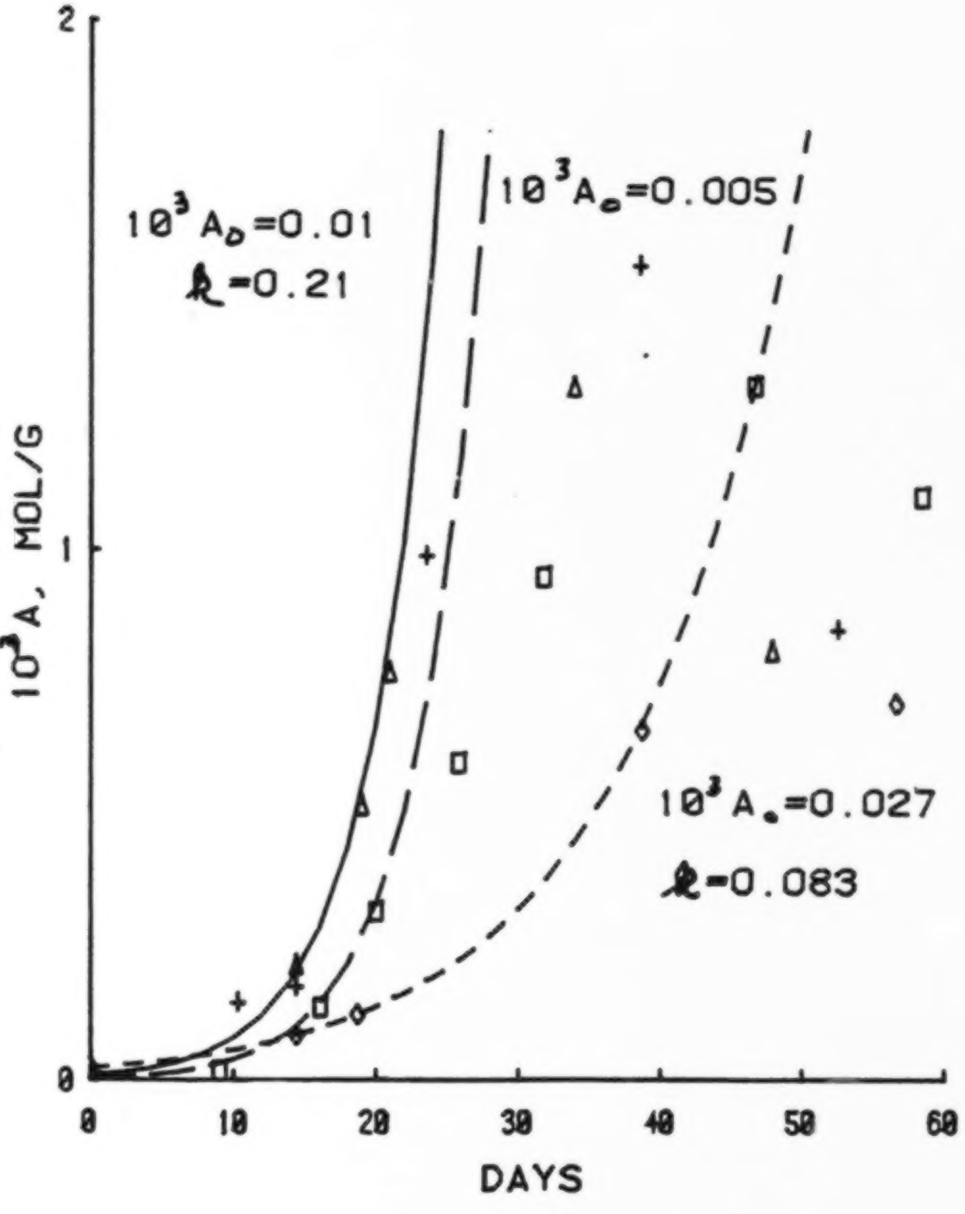


FIG. 10 ACID CONTENT VS DAYS AT 85 C AND 100 % RH
Δ, I/U=0; +, I/U=0.14;
□, I/U=0.55; ◊, I/U=1.1
LINES, $A=A_o EXP(kt)$

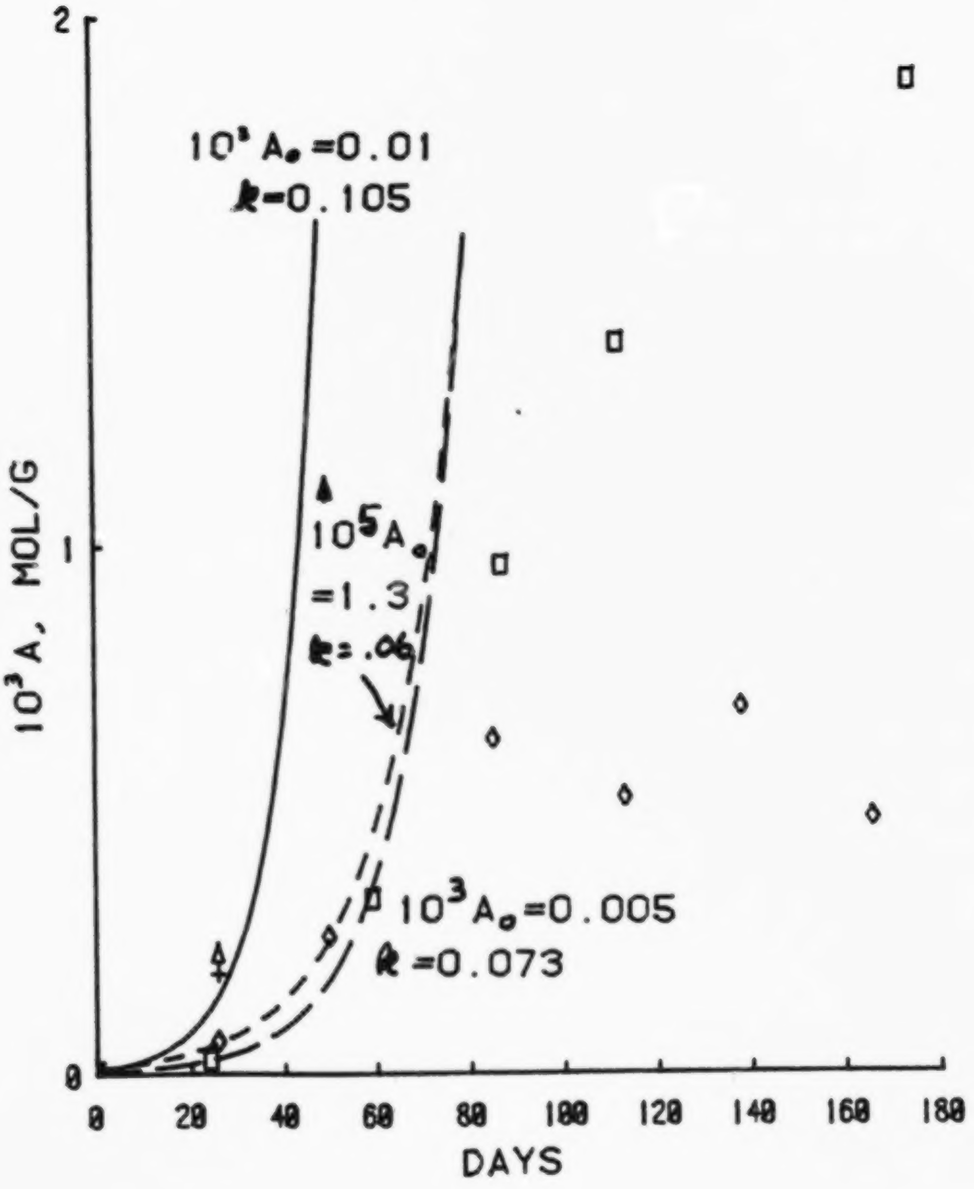


FIG. 11 ACID CONTENT VS DAYS AT
85 C AND 50% RH
Δ, I/U=0; +, I/U=0.14;
□, I/U=0.55; ◇, I/U=1.1
LINES, $A=A_0 \mathrm{EXP}(kt)$

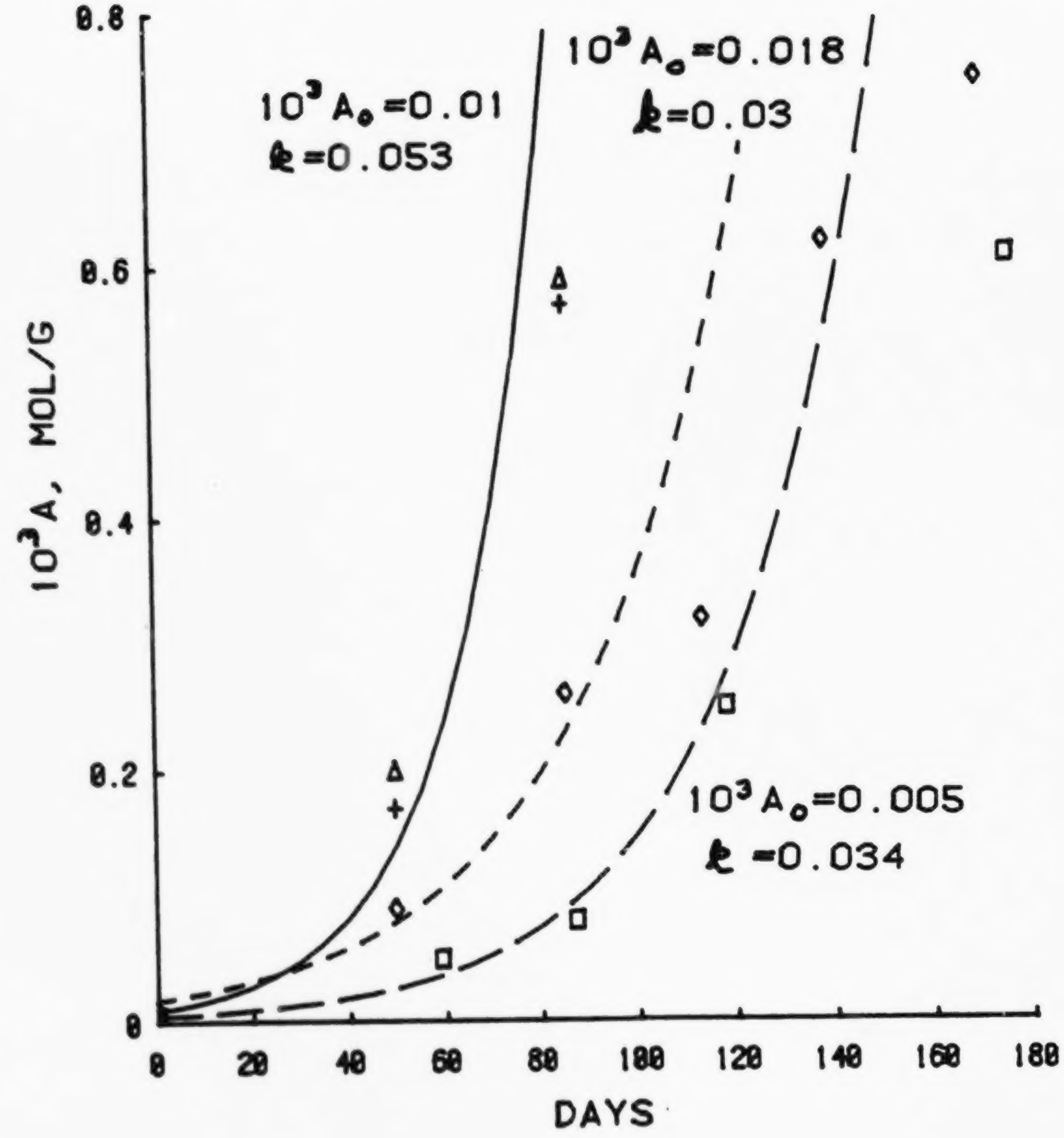


FIG. 12 ACID CONTENT VS DAYS AT 85 C AND 25% RH
△, $I/U=0$; +, $I/U=0.14$;
□, $I/U=0.55$; ◇, $I/U=1.1$
LINES, $A=A_o \mathrm{EXP}(kt)$

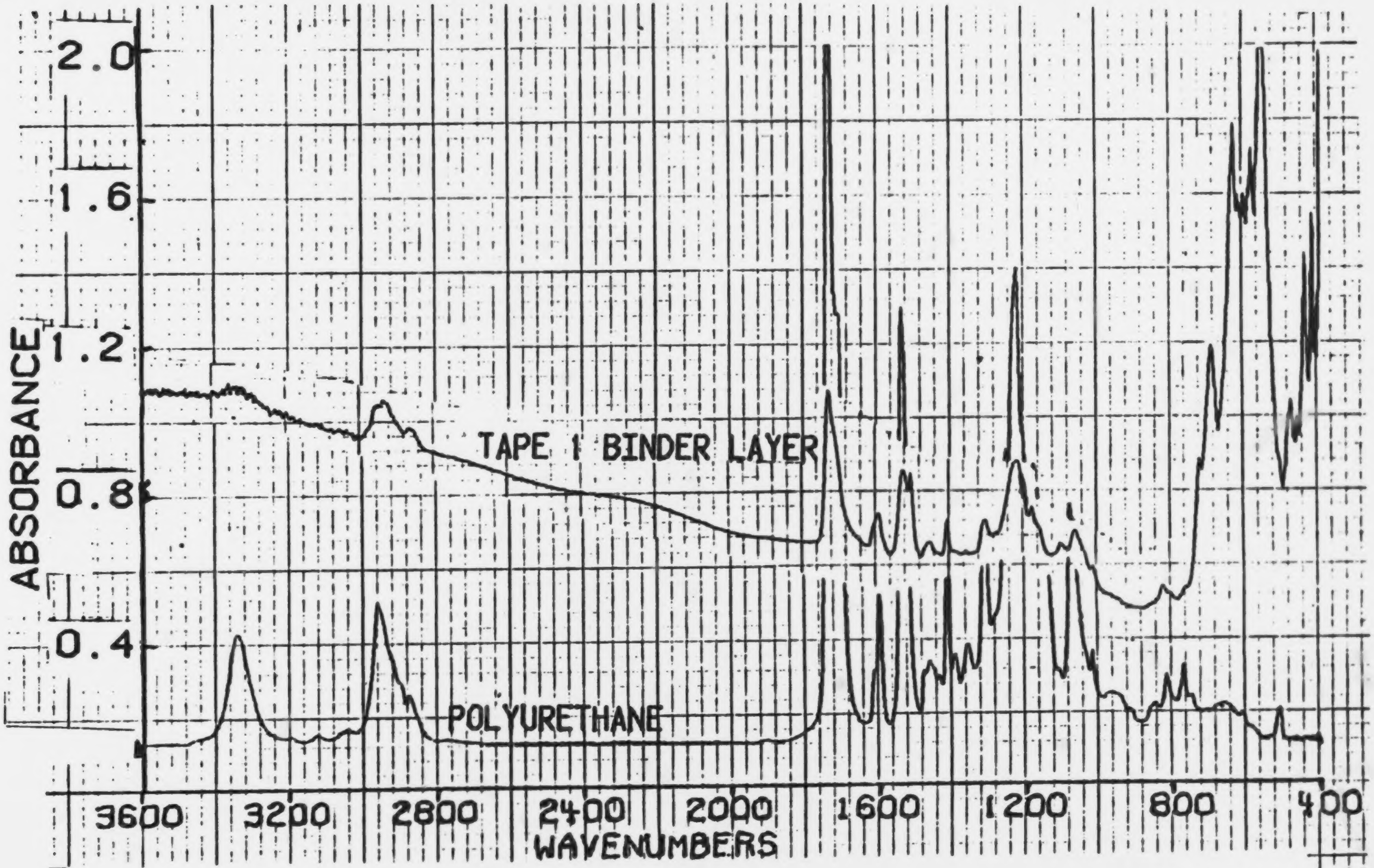


FIG 13 INFRA-RED SPECTRA OF BINDER LAYER AND POLYURETHANE

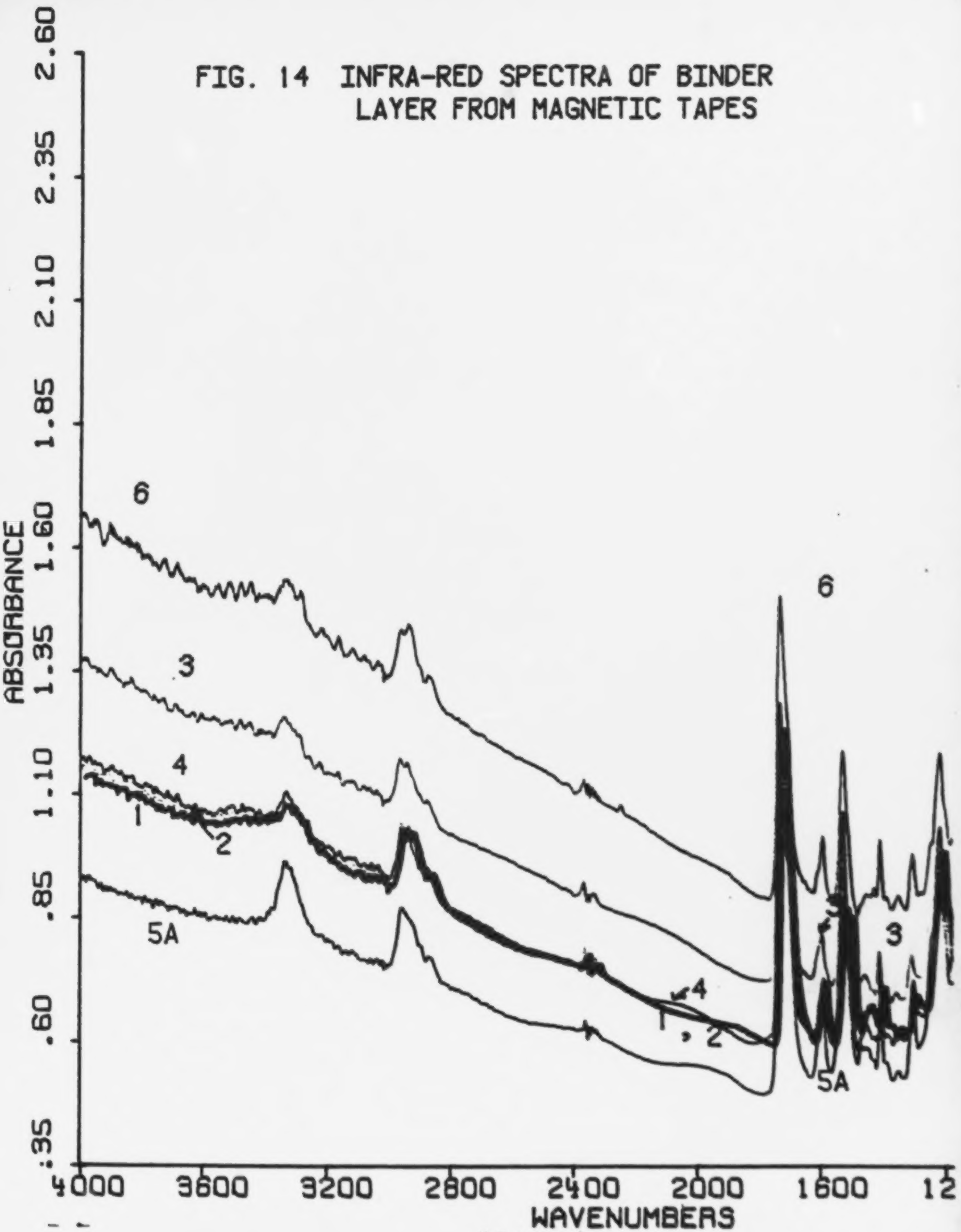


FIG. 14 INFRA-RED SPECTRA OF BINDER LAYER FROM MAGNETIC TAPES

FIG 15 TAPE EXTRACT AFTER AGING AT 60 C AND 100% RH

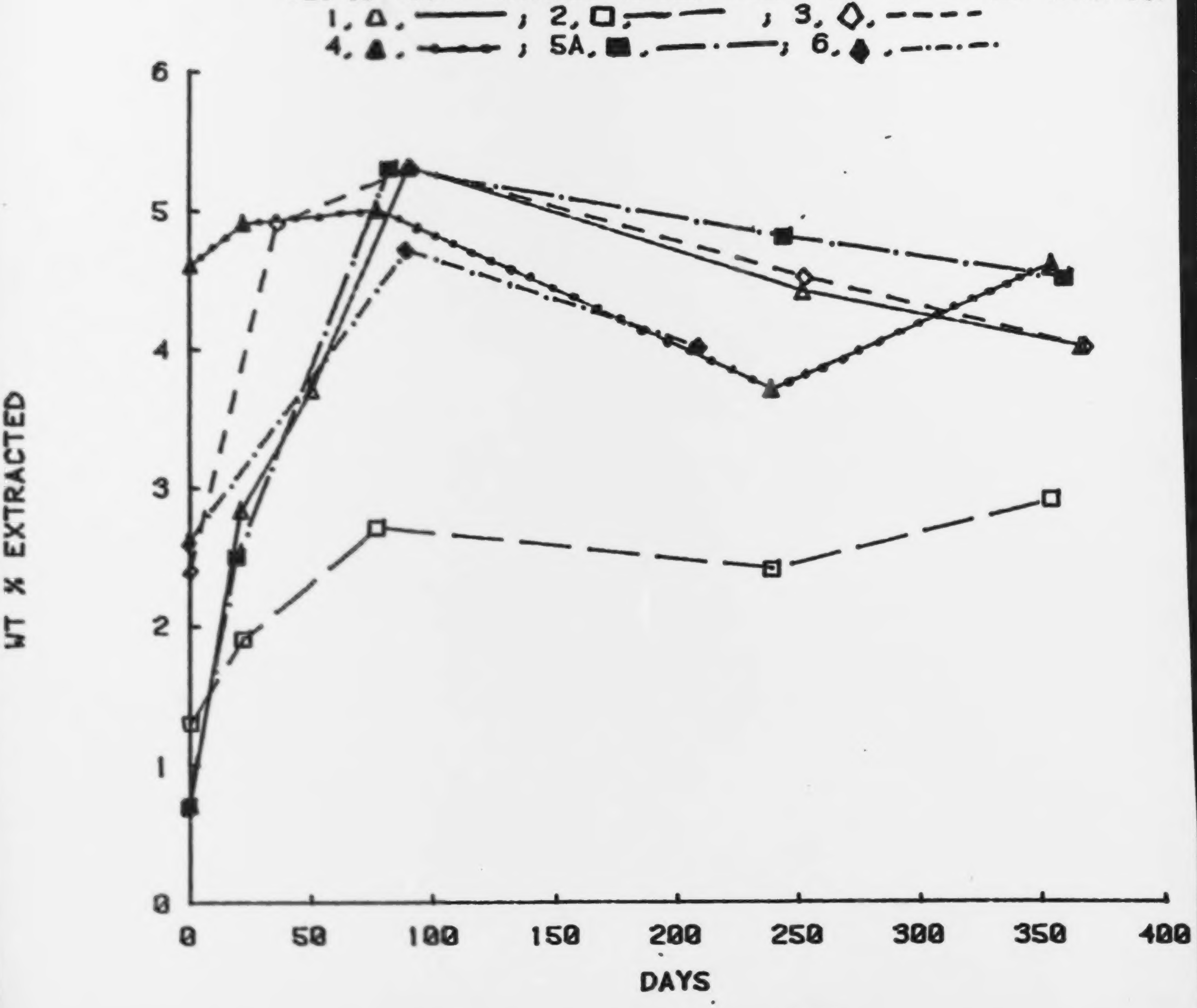


FIG. 16 RECORDER PLOTS DURING STRIPPING OF BINDER LAYER FROM TAPES 1, 5A, 5B

TAPE 1, FULL SCALE 500G;
TAPE 5A, 1KG FS; TAPE 5B, 200G FS

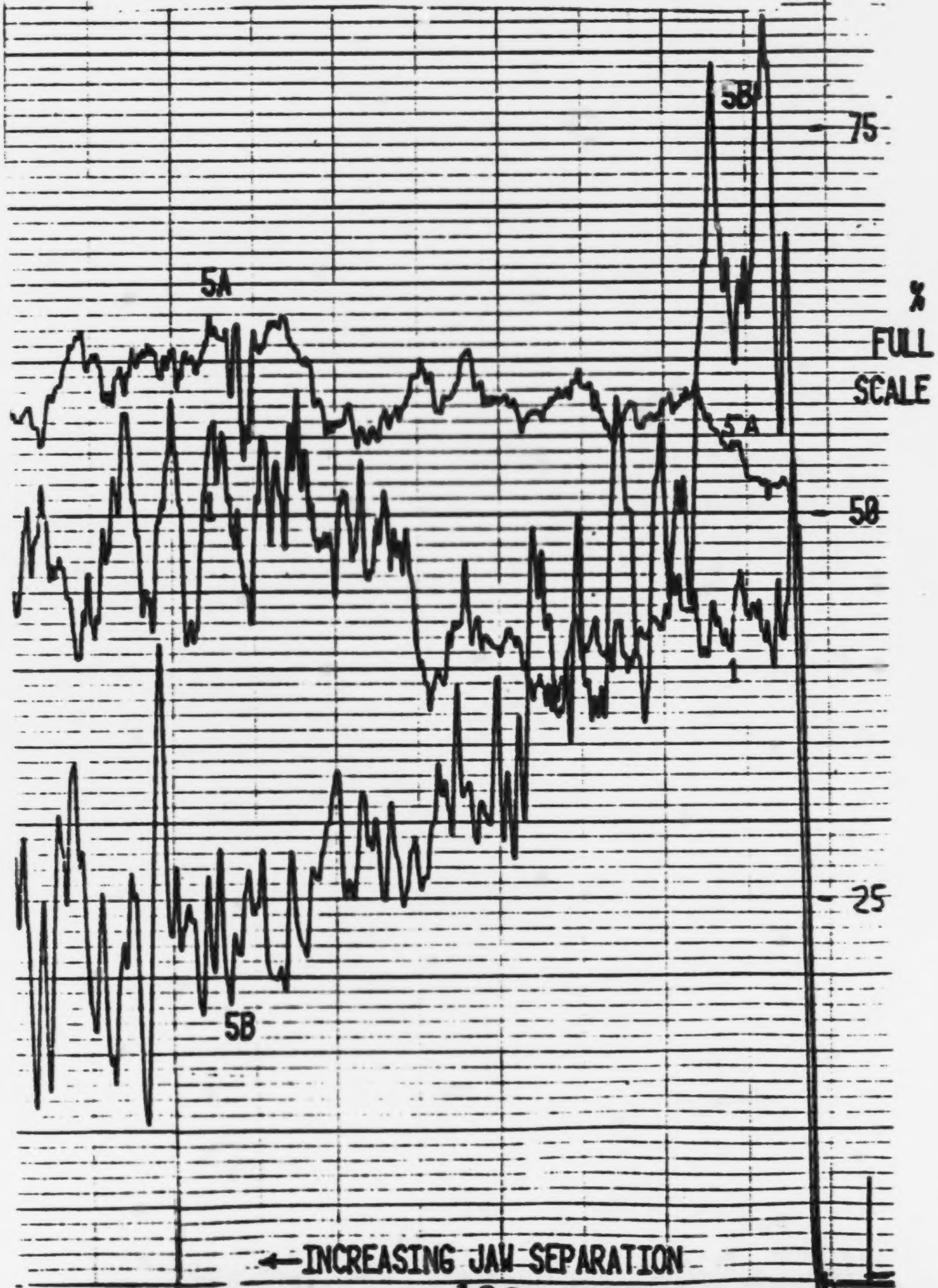


FIG. 17

STRIPPING PATTERNS OF BINDER LAYER

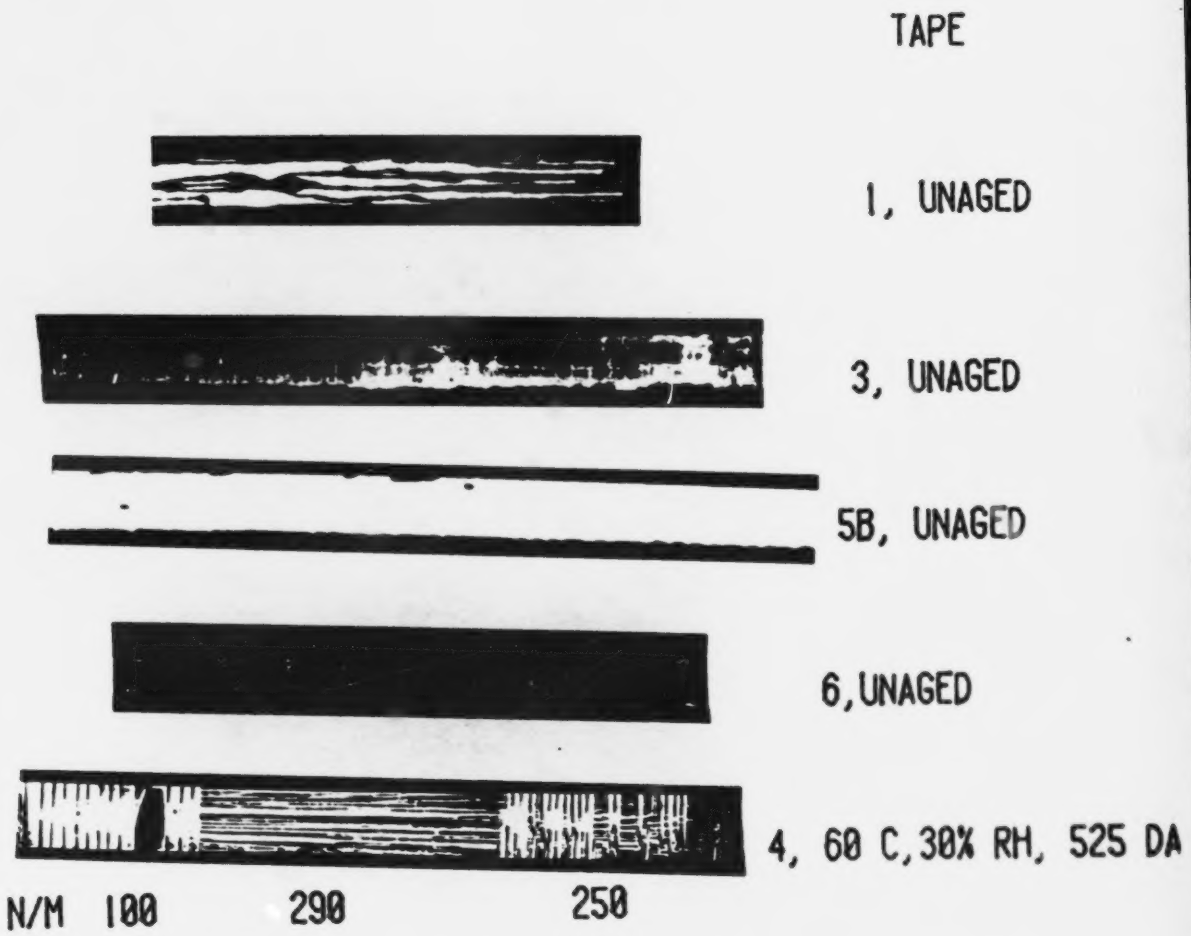


FIG 18 BINDER ADHESION AFTER AGING AT 60 C AND 30% RH

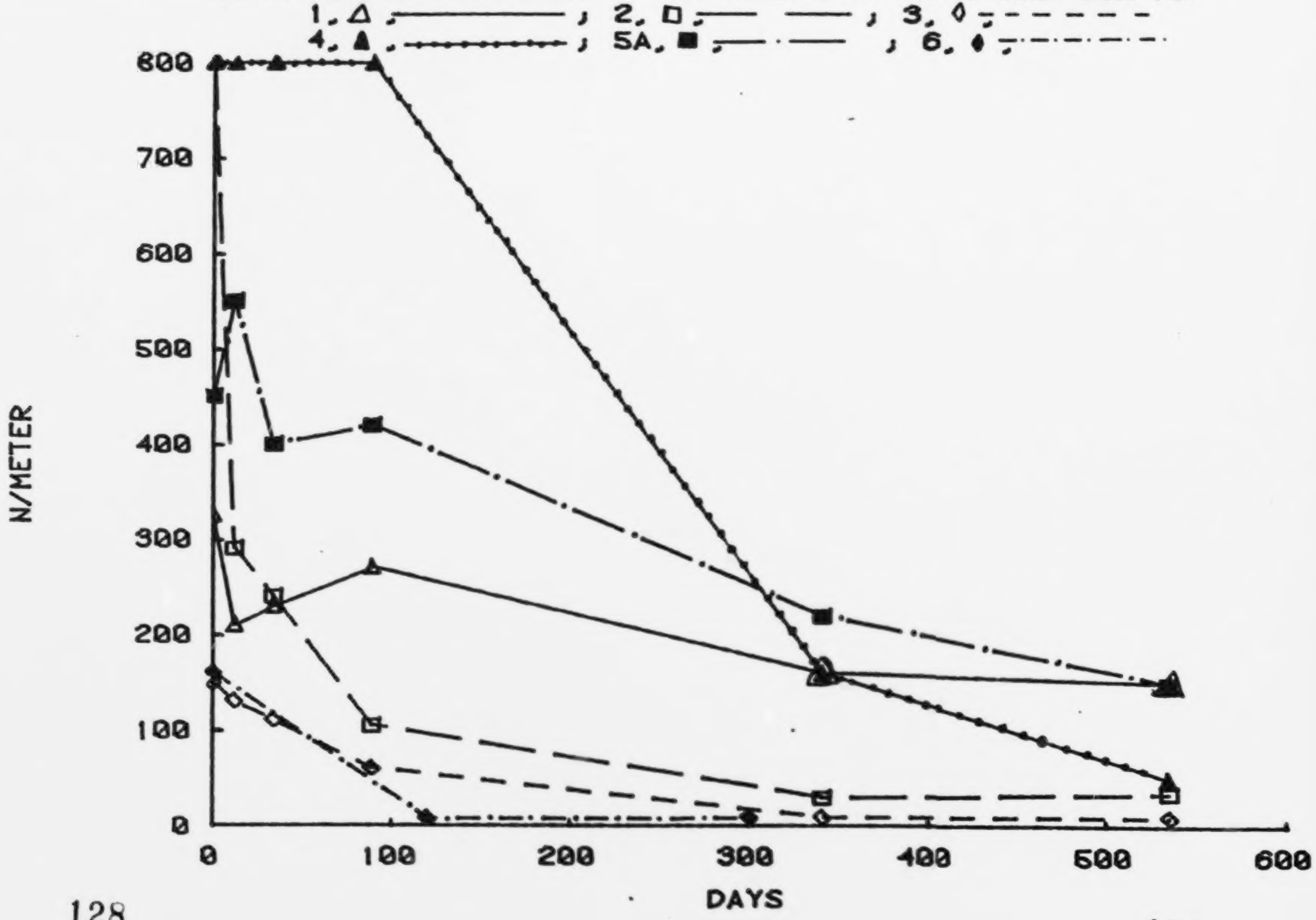
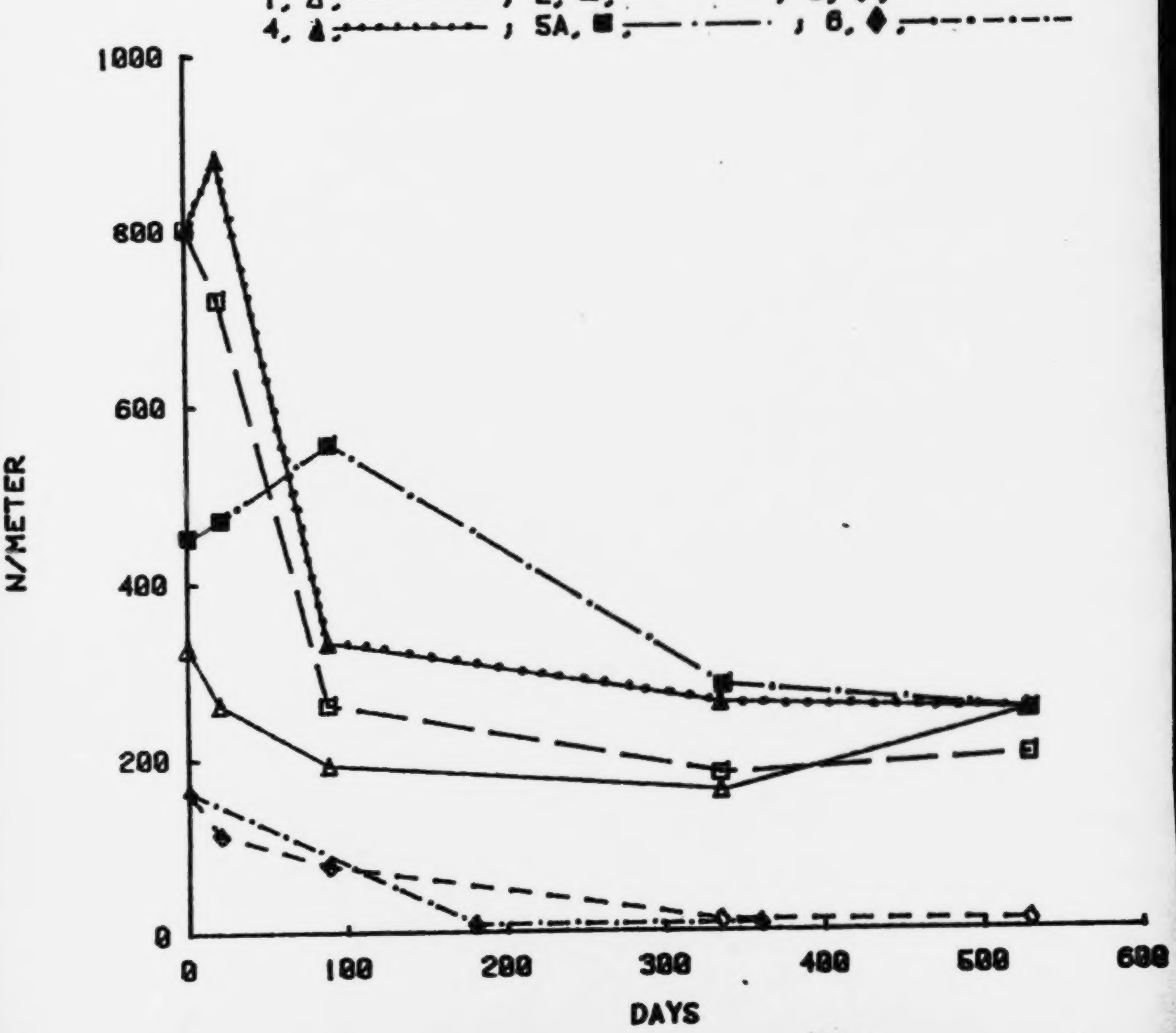


FIG 19 BINDER ADHESION AFTER AGING AT 60 C AND 15% RH



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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Aging studies with poly(ethylene terephthalate) film base indicate the lifetime is equal to about 1000 years if the material is stored at 20-25°C and 50% relative humidity. Concentration changes of acid and alcohol groups that occur as a result of aging have been measured by infrared analysis. Rate constants calculated by this method agree reasonably well with those calculated from acid contents determined by titration.

Crosslinked polyester polyurethanes were prepared as models of the binder of magnetic tape. Aging studies with these materials indicate that they hydrolyze more slowly than ordinary polyester polyurethanes. Samples aged at 85°C at 100, 50, and 25% relative humidity eventually deteriorated greatly in a physical sense.

Magnetic tapes were aged and measurements made of the sol content of the binder and its adhesion to the polyester base. The latter quantity appears to be a more valuable indicator of tape condition than sol content. Values of binder adhesion of six brands of magnetic tape initially varied between 800 and 35 N/m (or g/cm). Binder adhesion in aged tapes was less the higher the temperature and humidity of aging. A tape transport had difficulty processing tape with values of binder adhesion as low as 10 N/m. There was no problem at 35 N/m. It is anticipated that the lifetime of magnetic tapes can be predicted by measurements of binder adhesion.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Hydrolysis; magnetic tape; polyester; poly(ethylene terephthalate); polyurethane

13. AVAILABILITY

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